

SEP 14 1929

SOIL SCIENCE

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PUBLISHED MONTHLY
THE WILLIAMS & WILKINS COMPANY
MT. ROYAL AND GUILFORD AVENUES
BALTIMORE, MARYLAND, U. S. A.

Made in United States of America

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THE LAWS OF SOIL COLLOIDAL BEHAVIOR: I

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Received for publication April 2, 1929

The mineral fraction of the soil colloidal material which constitutes the residue of rock weathering is composed mainly of the hydrated oxides of silicon, aluminum, and iron together with certain proportions of alkaline and alkaline earth bases. This material exists in the soil normally in the form of a gel which is mixed with, and coats the coarser particles of silt, sand, and gravel. The quality and quantity of this gel has a profound influence upon the structure of the soil, its workability, and its waterholding power; upon the capillary and gravity movement of water; and upon the adsorptive and exchange capacity of the soil and its buffer action.

The composition of the colloidal material varies greatly and depends apparently upon genetic forces and climatic conditions, such as temperature and precipitation, rather than upon the composition of the parent rock (17). The following outstanding facts from the work of Robinson and Holmes (22) are of interest in this connection.

The higher the silica/sesquioxide ratio the higher the proportion of the mono- and divalent bases. The lower this ratio, that is, the higher the proportion of sesquioxides, the smaller the quantities of bases present. In general the high-ratio colloids are found in arid regions and the colloids with a low ratio occur chiefly in warm, humid regions.

The colloidal behavior varies greatly with the composition. Swelling, viscosity, dispersibility, heat of wetting, adsorption of bases and basic dyes, and base exchange are all manifested to a greater degree by the colloidal materials with a high silica/sesquioxide ratio than the materials in which this ratio is low (2, 13, 15). The materials with a high ratio are also more electronegative, as measured by the quantities of a basic dye or of a solution of AlCl_3 necessary to neutralize the negative charge of the particles (13, 18). Particles having a high proportion of silica and bases remain electro-negative in acid as well as in neutral and alkaline solutions, whereas a high proportion of sesquioxides leads to an amphoteric behavior, the particles becoming electro-positive in acid solutions (13). The author has further shown that in agreement with this behavior the materials high in sesquioxides adsorb appreciable quantities of anions such as Cl and SO_4 from acid but not from neutral solutions (16).

The colloidal behavior of a given soil material has been shown by Gedroiz (8) to be greatly influenced by the nature of the exchangeable cations present.

The author has recently established a quantitative relationship between the points of maximum swelling and the base exchange capacity in the case Na-saturated soil colloids (15). It was also shown that a gradual increase of Na and a corresponding decrease of Ca (the sum of the two ions being kept constant and equal to the exchange capacity) increased the negative charge, the dispersibility, and the swelling to a maximum. The enormous swelling of certain bentonites which is ascribed to a micaceous structure ["one dimensional colloid" (1)] was shown to be due to the nature of the exchangeable cations. When electrodialyzed, the bentonite lost its abnormal power to swell but regained this power after saturation with NaOH.

NEGATIVE ADSORPTION

In a study of the adsorption of anions by soil colloids of varying silica/sesquioxide ratio, the adsorption of the Cl and SO₄ ions was always found to

TABLE 1
Negative adsorption of the Cl ion by Na- K- Ca- and Ba-saturated Sharkey soil colloid

TREATMENT	CONCENTRATION OF Cl IONS		DIFFER- ENCE	ELECTRICAL MIGRATION
	Original solution	Superna- tant liquid		
	N	N	N	$\mu/\text{ec.}$ 1 volt/cm.
Na-saturated.....	0.2002	0.2095	0.0093	-3.1
K-saturated.....	0.2004	0.2058	0.0054	-1.7
Ca-saturated.....	0.1979	0.2010	0.0031	-0.6
Ba-saturated.....	0.1998	0.2020	0.0022	-0.4

be negative in neutral and alkaline solutions. The magnitude of this negative adsorption was then measured. Five-gram samples of Na-, K-, Ca- and Ba-saturated Sharkey soil colloid were shaken each with 50 cc. 0.2 N solution of the respective chloride. The Cl ion was determined in the supernatant liquid after standing 3 days. The results are given in table 1. [For details see original paper (16).] The last column gives the cataphoretic movement of the particles.

The experiment shows that the different cations cause a negative adsorption of the Cl ion which varies in the same order as was previously found in the case of swelling and dispersibility. One is at once reminded of the work of Procter and Wilson (20, 21) and especially of the work of Loeb (12) on the colloidal behavior of the proteins. If a definite relationship between the negative adsorption and the colloidal behavior of soil materials could be established the problem would be placed on a quantitative basis. We shall see that this is to a certain extent possible.

The fact that the charge, as measured by cataphoresis, is highest in the case of the Na-saturated particles indicates that this ion dissociates most extensively

from the surface of the particles while the Ba ion dissociates the least. The electronegative soil particle or micelle is therefore surrounded by a swarm or atmosphere of cations. This, the so-called outer layer of ions in the Helmholtz double layer, is not to be looked upon as a layer in the form of a concentric shell, but rather as being diffuse, as suggested by Gouy (9). The distribution of the ions in the outer layer must be similar to the distribution of the gas molecules in the atmosphere or to the distribution of colloidal particles, as found by Perrin (19). In these cases equilibrium is established when the effect of gravity equals the osmotic pressure (or Brownian movement in the case of colloidal particles). For gases this is expressed by the formula

$$h = \frac{RT}{gM} \ln \frac{P_0}{P} \quad (4)$$

where h is the height, P_0 the pressure at the bottom, P the pressure at height h , g the acceleration due to gravity, and M the molecular weight. In the case of ions dissociated by the colloidal micelle, equilibrium will be established when the electrostatic attraction of the inner layer equals the osmotic pressure of the dissociated ions. If this attraction were substituted for the force of gravity in the preceding equation, a similar expression would be obtained, according to which the concentration of the ions in the outer layer should decrease in geometric progression as the distance from the inner layer increases in arithmetic progression. Evidence in support of this theory will be presented later in this paper but the experiments of Bouyoucos and McCool (5), who found that as the water content of the soil decreases in an arithmetic progression the freezing point depression increases in a geometric progression, may be alluded to at this point.

From the migration velocities of the particles saturated with different bases, it is evident that the dissociation of the cations depends not only upon the valence but also upon other factors, among which atomic volume and the degree of hydration of the ions appear to be the most important, as has been shown by Wiegner (23). The smaller the volume of the cation the greater the hydration, and the greater the number of water molecules attached to the ion the smaller its potential and the more insensible therefore to the electrostatic pull from the surface. The higher the valence and the lower the hydration, on the other hand, the more easily the ion is attracted to the inner layer of opposite sign of charge. For each ion there appears to be a limiting potential in the double layer above which the ion cannot exist in the dissociated condition. It is significant that this limiting potential never exceeds the potential of the single common ions themselves, which is estimated by von Hevesy (10) to range about 70 millivolts. The potential calculated for the fastest moving soil particles saturated with NaOH was found to be about 56 millivolts, which corresponds to a migration velocity of 4μ per second in a potential gradient of 1 volt per cm. (15). Particles saturated with bases of higher molecular weight and valence always move slower, and this is true in cases where no excess base is added and

in the absence of other electrolytes. This is stated to preclude any argument that the effect is due to a Donnan equilibrium.

That the Donnan distribution depends only on the valence is a mathematical truth which no one will dispute. But the primary cause of certain colloidal behaviors, namely, the formation of an atmosphere of ions around a colloidal particle, is entirely independent of the Donnan equilibrium. The density and thickness of this ionic atmosphere or layer must be governed by the specific nature of the ions composing it. The Donnan distribution, which is an effect rather than a cause, does not enter until we have an excess of electrolyte (which is of course always the case to a certain extent, because of hydrolysis and the OH and H ions of the water).

On the basis of the foregoing theory we can easily account for the enormous swelling, or to be more exact—the imbibition of water, of the colloidal material when just saturated with NaOH (neutral reaction). The cation of this base remains highly dissociated. This causes a high osmotic pressure in the immediate neighborhood of the particles. Water is imbibed, or, what amounts to the same thing, the ions move farther away from the surface. This continues until there is an equilibrium between the electrostatic attraction and the osmotic pressure. The gel has attained a maximum in swelling. The same line of reasoning will explain why the electrokinetic potential is at a maximum when the material is just saturated with base. The law relating the charge e to the potential ζ of concentrically charged spheres of radius r and r_1 is

$$\zeta = \frac{e (r_1 - r)}{D r r_1} \quad (B)$$

For the potential of the double layer of colloidal particles, this is written

$$\zeta = \frac{e \vartheta}{D r (r + \vartheta)} \quad (C)$$

where D is the dielectric constant of the medium and ϑ is the "thickness" of the double layer, or the mean distance between the two layers.

THE HOFMEISTER SERIES

From this expression it is evident that the greater the number of charges, that is, the greater the number of ions of one sign of charge in excess of the number of ions of opposite charge, in the two layers the greater is the potential difference between them. Also the further away from the inner layer the ions of the outer layer are able to diffuse before equilibrium is established between the electrostatic and the osmotic forces, the greater also is the ζ . The different ability of the ions to diffuse into the outside medium against the electrostatic attraction depends upon the specific nature of the ions, such as hydration and valence. It

is undoubtedly in this relationship that the ions arrange themselves in the well-known Hofmeister or lyotropic ion series.

Loeb denies emphatically the existence of such ion series as far as the proteins are concerned, and others are attacking the work of Loeb because of this denial. It seems to the writer that there need be no conflict between the laws governing the Donnan equilibrium and the Hofmeister ion series. Both are independent of each other and both may be coexistent. It seems that the cart has been put before the horse. The Donnan distribution of the free electrolyte is an effect rather than a cause in colloidal behavior. The Donnan equilibrium is governed by another equilibrium which precedes it, namely, the equilibrium between the colloidal micelle and its ions. In view of the great differences in dissociation, solubility, and hydration, in common compounds, it would seem absurd to assume that all ions would bear the same relation to the colloidal micelle. The equilibrium between micelle and its ions must be governed by the specific nature of both. That the migration velocity is greater in the Na-saturated than in the K-saturated particles and that the velocity of the Ca-saturated is greater than the velocity of the Ba-saturated particles must depend upon differences in the nature of the ions. The atmosphere of Na ions extends farther out than the atmosphere of the K ions. The potential and also the quantity of water held by osmotic forces (the swelling) are correspondingly greater in the case of the Na-saturated particles. The same thing applies to the differences between any other pair of base-saturated colloids.

As an outside electrolyte enters into the system, a Donnan distribution is established, as measured in the foregoing case by the negative adsorption, and this will vary in the same order as the potential and the swelling. The addition of an electrolyte suppresses the potential, the swelling, and the inequality (the value of $\frac{x}{y}$) of the Donnan distribution.

The laws governing the Donnan equilibrium will be very briefly discussed here, the uninitiated reader being referred to original sources (6, 12). But instead of making use of the conventional membrane which separates a non-diffusible ion from the rest of the system, the case of a colloidal micelle will be here considered.

As an example, consider a colloidal particle saturated with NaOH and suspended in pure water and assume the entire absence of free electrolytes (a condition which is of course never realized). Some of the Na ions will dissociate and diffuse into the water until the backward electrostatic pull just balances the osmotic tendency of the ions to distribute themselves equally in all parts of the system. An ion atmosphere has been formed around the particle within which the water is osmotically held, is more or less rigid, and must therefore move with the particle to which it belongs. The particle, its atmosphere of ions, and its imbibed water constitute the colloidal micelle. Within this micelle

the intensity of the electric fields, and therefore the potential gradient, will vary as we pass from one to the other of the following phases of the system.

interior of	interfacial	inner	outer layer	outside
particle	layers of	layer	or ion	liquid
	molecules	of ions	atmosphere	

The potential difference in the double layer, which depends on the number of ions dissociated and on the thickness of the atmosphere, will, like the imbibition, be at a maximum. The P.D. (potential difference) between the interior of the atmosphere and the outside water will likewise be at a maximum.

THE DONNAN EQUILIBRIUM

Now let an electrolyte like NaCl be added to the suspension and let us consider the Donnan distribution of ions between the micellar solution (inside the ion atmosphere) and the inter-micellar or outside solution after equilibrium has been established. The principle of a constant ion product demands that

$$[\text{Na}^+][\text{Cl}^-]_{\text{outside}} = [\text{Na}^+][\text{Cl}^-]_{\text{inside}}$$

where the brackets signify concentration.

If this equation is to hold it is evident that fewer of the Na and Cl ions will have distributed themselves inside the Na-ion atmosphere than in the outside solution. This is best expressed by the general equation for the Donnan equilibrium for monovalent ions

$$x^2 = y(y+z) \quad (D)$$

where, in application to the above case, x is the chloride, cation, and anion concentration in the (outside) intermicellar solution; y is the concentration of the same ions inside the micellar ion atmosphere; and z is the concentration of the Na ions of the micellar atmosphere dissociated by the colloidal particle.

In this expression $x > y$, that is, the Na and Cl ions must be "negatively adsorbed" by the soil colloidal material, as was shown in table 1, and the negative adsorption must be greater the greater the value of z , that is, the greater the number of ions dissociated by the colloidal particle.

If the values of x and y can be determined, z may be calculated

$$z = \frac{(x+y)(x-y)}{y} \quad (E)$$

when all ions are monovalent.

Loeb has shown that the P.D. across a membrane separating a non-diffusible ion from an outside solution containing no such ions is reduced by the addition of an electrolyte. It can similarly be shown that the P.D. between the interior

of the micellar atmosphere and the outside liquid must be suppressed by the addition of an electrolyte. By inserting the values of $\frac{x}{y}$, as determined by the Donnan equilibrium, in the Nernst formula we get

$$\text{P.D.} = \frac{R}{a} \frac{T}{F} \ln \frac{x^a}{y^a} = \frac{R}{F} T \ln \frac{x}{y}$$

where a is the valence.

By substituting the common in place of the natural logarithms and writing the numerical value for $\frac{R}{F} T$ at room temperature we get

$$\text{P.D.} = 58 \log \frac{x}{y} \text{ millivolts} \quad (F)$$

Now since the value of $\frac{x}{y}$ depends upon the magnitude of z as well as on the concentration of the added electrolyte, the effect of the latter on the P.D. can best be illustrated by writing $\frac{x}{y}$ in terms of y and z . When all the ions in the Donnan equilibrium have the same valence then

$$x^2 = y(y+z)$$

and

$$x = \sqrt{y(y+z)}$$

Substituting this value for x in the term $\frac{x}{y}$, we get

$$\frac{\sqrt{y(y+z)}}{y} = \sqrt{\frac{y+z}{y}} = \sqrt{1 + \frac{z}{y}}$$

Formula (F) then becomes

$$\text{P.D.} = \frac{58}{2} \log \left(1 + \frac{z}{y} \right) \text{ millivolts} \quad (G)$$

From this formula it is evident that the greater the concentration of electrolyte added, that is, the greater the value of y , z remaining constant, the greater the suppression of the P.D.

THE VALENCE EFFECT

Let us now see how a difference in the valence of the ions must, according to theory, affect the distribution of the ions between the micellar and intermicellar

solutions and, by virtue of this distribution, to what degree a suppression of the above discussed P.D. is brought about.

The difference in valence effect will depend on which of the ions of the added electrolyte has the higher valence. If this be the ion which has the opposite sign of charge to that of the colloidal particle the effect will be greater, while if it be the ion with the same sign of charge the effect will be smaller than in the case where all ions involved are monovalent.

The first case may be illustrated by considering the effect of CaCl_2 on a Ca-saturated soil colloid. (The Ca-saturated material is considered in this case so as to have a common ion and thus avoid complications.)

Let x be the molar concentration of Cl ions in the outside solution, y the concentration of the Cl ions in the micellar solution; then $\frac{x}{2}$ and $\frac{y}{2}$ will be the corresponding concentrations of the Ca ions of the free CaCl_2 while the concentration of Ca ions dissociated by the colloidal particle in the micellar solution becomes $\frac{z}{2}$. Since CaCl_2 dissociates into two Cl ions and one Ca ion, the Donnan equilibrium becomes in this case

$$x^2 \frac{x}{2} = y^2 \frac{(y+z)}{2} \quad (H)$$

$$x^3 = y^2 (y+z)$$

$$x = \sqrt[3]{y^2 (y+z)}$$

Expressing $\frac{x}{y}$ in terms of y and z we get

$$\frac{x}{y} = \frac{\sqrt[3]{y^2 (y+z)}}{y} = \sqrt[3]{\frac{y+z}{y}} = \sqrt[3]{1 + \frac{z}{y}}$$

and formula (F) becomes in this case

$$\text{P.D.} = \frac{58}{3} \log \left(1 + \frac{z}{y} \right) \text{ millivolts} \quad (I)$$

By comparing formula (G) and (I) it will be seen that, at the same values of y and z , the P.D. between the micellar and the outside solution in the case of an electronegative colloid will be only $\frac{2}{3}$ as great when the cation of the added electrolyte is divalent and the anion is monovalent as when both ions are monovalent. This difference is merely due to the suppressing effect of the added electrolyte and has nothing to do with the actual difference in P.D. in the case of the Ca- and Na-saturated colloid. The P.D. in the case of the Na-saturated particles is much higher at the outset, that is, the value of z is greater because of a greater dissociation of Na ions into the micellar atmosphere, as already pointed out.

Let us now consider the second case, namely, the effect of an electrolyte with a divalent ion having the same sign of charge as that of the colloidal particle while the other ion is monovalent. The effect of Na_2SO_4 on the Na-saturated soil colloid may be considered as an example. If x be the molar concentration of Na ions in the outside solution, y the concentration of Na ions of the Na_2SO_4 in the micellar solution; then $\frac{x}{2}$ and $\frac{y}{2}$ will be the corresponding concentrations of the SO_4 ions while z represents the concentration of the Na ions dissociated by the particle. The equilibrium equation then becomes

$$x^2 \frac{x}{2} = \frac{y}{2} (y + z)^2 \quad (J)$$

$$x^3 = y (y + z)^2$$

$$x = \sqrt[3]{y (y + z)^2}$$

substituting $\sqrt[3]{y (y + z)^2}$ for x in $\frac{x}{y}$, we get

$$\frac{\sqrt[3]{y (y + z)^2}}{y} = \sqrt[3]{\frac{(y + z)^2}{y^2}}$$

and formula (F) becomes in this case

$$\text{P.D.} = \frac{58}{3} \log \frac{(y + z)^2}{y^2} \text{ millivolts} \quad (K)$$

with the same values for y and z , this formula gives a P.D. which bears the same ratio to the P.D. given by formula (G) as 1.33 to 1.00. Na_2SO_4 will therefore suppress the P.D. less than NaCl. The addition of an electrolyte with an anion having a still higher valence will lead to a still lesser suppression of the P.D. For $\text{Na}_3\text{Fe}(\text{CN})_6$ and $\text{Na}_4\text{Fe}(\text{CN})_6$ the above expression for $\frac{x}{y}$ becomes

$$\sqrt[4]{\frac{(y + z)^3}{y^3}} \text{ and } \sqrt[5]{\frac{(y + z)^4}{y^4}}$$

respectively.

This negative influence upon the suppression of the P.D. and, as we shall see later, upon other properties as well, which must be encountered whenever the valence of the ion of the same sign of charge as that of the colloid is higher than the valence of the other ion has apparently been overlooked by Loeb. He considers only the cases represented by formula (G) and (I) in which the term $\log \left(1 + \frac{z}{y}\right)$ occurs and denies repeatedly that the ion of the same sign of charge as the colloid exerts any influence whatsoever (12, p. 203, 246). He states "that

whenever a salt depresses any physical property of a protein (or a colloidal solution in general) this action is due to that ion of the salt which has the opposite sign of charge to that of the protein ion." Further (p. 204) that "the term, $\log \left(1 + \frac{z}{y}\right)$ derived from the (Donnan) equilibrium equation makes the P.D. a function of z and y , i.e., that ion which has the opposite sign of charge to that of the protein ion."

But it is evident that according to Nernst formula (*F*) the P.D. is a function of

$$\frac{(\text{Cl}^-) \text{ outside}}{(\text{Cl}^-) \text{ inside}} = \frac{(\text{Na}^+) \text{ inside}}{(\text{Na}^+) \text{ outside}} = \frac{x}{y} = \frac{y+z}{x}$$

in the case of NaCl in equilibrium with the Na-saturated colloid. The P.D. is therefore a function of the relative distribution of either ion and this distribution varies, as we shall see, with the valence of either ion. The term $\left(1 + \frac{z}{y}\right)$ represents a special case derived from the value of $\frac{x}{y}$ in the equilibrium equation in the case of certain valence combinations [formulas (*D*) and (*H*)]. In other valence combinations $\frac{x}{y}$ in terms of y and z assumes different forms, as has been shown.

Curiously enough the experimental work of Loeb on the proteins, excepting certain data on anomalous osmosis and a few other cases, appears to support his contentions. In his paper on electrical charge and anomalous osmosis, he suggests however that salts with trivalent cations and tetravalent anions form "loose compounds with isoelectric gelatin" (11, p. 486).

Formula; (*F*) shows the P.D. to be a function of $\frac{x}{y}$ independently of the valence, whereas formulas (*G*), (*I*), and (*K*) show how the P.D. varies with the valence at given concentrations of y and z . It becomes evident therefore that the value of $\frac{x}{y}$ must be different in each of the cases presented. In other words, the distribution of the different ions in the Donnan equilibrium must be more or less unequal depending upon the valence, that is, the observed negative adsorption of a non-reaching ion will vary with the valence according to a definite rule.

The theoretical relationship between valence and the Donnan distribution is shown in table 2.

The first column in the table shows the condition of the colloid, which is assumed to be saturated with and dissociating the same cation as that of the salt added, as shown in the second column. The third column shows the corresponding equilibrium formulas. The fourth column gives the formulas by which the P.D. is calculated, whereas the fifth column gives the P.D ratios

as far as they are governed by the Donnan equilibrium alone. The sixth column gives the distribution ratios of the ions of the salt between the micellar and intermicellar solutions when $y = z$.

The distribution ratios bring out the relation that the higher the valence of the anion (the valence of the cation remaining the same) the greater the relative concentration of the added electrolyte outside the micellar solution as compared to the concentration inside this solution. An increase in the valence of the cation (the valence of the anion remaining the same) has the opposite effect. In the former case the negative adsorption is increased; in the latter case it is decreased. It will be shown later that this relationship actually exists in the case of soil colloids.

TABLE 2

Theoretical relationship between valence, P.D. and ion distribution as demanded by the Donnan equilibrium between the micellar and intermicellar solution in an electronegative soil colloid

CONDITION OF COLLOID	GENERAL FORMULA OF SALT ADDED	EQUILIBRIUM FORMULA	P.D. IN MILLIVOLTS =	P.D. RATIOS	DISTRIBUTION RATIOS $\frac{z}{y}$ when $y = z$	$\frac{z}{y}$ LOG
M ^{'''} -saturated....	M ^{'''} A ₃ '	$x^4 = y^3 (y + z)$	$\frac{58}{4} \log \left(1 + \frac{z}{y} \right)$	0.500	1.190	0.075
M ^{''} -saturated.....	M ^{''} A ₂ '	$x^3 = y^2 (y + z)$	$\frac{58}{3} \log \left(1 + \frac{z}{y} \right)$	0.666	1.259	0.100
M ['] -saturated.....	M ['] A'	$x^2 = y (y + z)$	$\frac{58}{2} \log \left(1 + \frac{z}{y} \right)$	1.000	1.414	0.150
M ['] -saturated.....	M ₂ ' A''	$x^3 = y (y + z)^2$	$\frac{58}{3} \log \frac{(y + z)^2}{y^2}$	1.333	1.587	0.200
M ['] -saturated.....	M ₃ ' A'''	$x^4 = y (y + z)^3$	$\frac{58}{4} \log \frac{(y + z)^3}{y^3}$	1.500	1.682	0.225
M ['] -saturated.....	M ₄ ' A''''	$x^5 = y (y + z)^4$	$\frac{58}{5} \log \frac{(y + z)^4}{y^4}$	1.600	1.741	0.241

THE THEORY OF SWELLING AND THE INFLUENCE OF VALENCE

It was suggested in the foregoing that the enormous imbibition of water (swelling) exhibited by the NaOH-saturated soil colloids is due to a greater dissociation, or, what amounts to the same thing, to a weaker association with the colloidal complex of this cation. As a particle becomes saturated with NaOH the density and therefore the osmotic pressure of the ion atmosphere reaches a maximum. This explains the maximum swelling at that point. If an excess of base or any other electrolyte is added the swelling is suppressed. It will be shown that this suppression of the swelling is governed by the valence as well as by the concentration. The Donnan equilibrium will account for this influence. Loeb, who has established a definite relation-

ship between the concentration of the free electrolyte and the swelling of proteins, admits no other influences of valence than that of the ions having an opposite sign of charge to that of the colloid. It will be shown first, that, according to theory, the valence of both ions must influence the suppression of the osmotic pressure and swelling brought about by the addition of an electrolyte. Later, it will be shown that this double influence actually exists in the case of soil colloids.

Let us first consider the addition of NaCl to the Na-saturated colloid. The equilibrium equation then becomes

$$x^2 = y(y + z)$$

It is evident that $y < x$, that $(y + z) > x$, and also that the sum of the unequals is greater than the sum of the equals, thus

$$2y + z > 2x$$

The excess ion concentration in the micellar solution above that of the outside solution is therefore

$$2y + z - 2x \quad (L)$$

Since $2x > 2y$ it follows that

$$2y + z - 2x < z$$

the addition of the salt has therefore decreased the difference in osmotic pressure between the micellar and intermicellar solutions. The greater the concentration of the salt solution added the smaller the difference in osmotic pressure between the two phases. Loeb makes this very obvious, by putting

$$x = \sqrt{y^2 + yz} \text{ or } 2x = \sqrt{4y^2 + 4yz}$$

and

$$2y + z = \sqrt{4y^2 + 4yz + z^2}$$

when the difference becomes

$$\sqrt{4y^2 + 4yz + z^2} - \sqrt{4y^2 + 4yz}$$

from which it is readily seen that the difference decreases as y increases with the increase in salt added.

If the excess of molar concentration of ions in the micellar solution above that of the outside solution is represented by e , then

$$2y + z = e + 2x$$

When y and x equal zero $z = e$; the osmotic pressure and the swelling are therefore at a maximum in the absence of free electrolytes. Let us now consider

the influence of a salt in which the ion of the opposite sign of charge to that of the colloid is bivalent. The addition of CaCl_2 to the Ca-saturated colloid will serve as an example. The equilibrium equation then becomes

$$x^2 \frac{x}{2} = y^2 \frac{(y+z)}{2} \quad (H)$$

Since x and y represent the molar concentrations of the Cl ion outside and inside the micellar solution respectively, $\frac{x}{2}$ and $\frac{y}{2} + \frac{z}{2}$ will be the corresponding Ca-ion concentrations. The excess ion concentration in the micellar solution above that of the outside solution is therefore

$$e = 3/2 y + \frac{z}{2} - 3/2 x. \quad (M)$$

As an example of the influence of a bivalent ion having the same sign of charge as that of the colloid, the addition of Na_2SO_4 to the Na-saturated colloid may be given. The equilibrium equation becomes then, as already shown

$$x^2 \frac{x}{2} = \frac{y}{2} (y+z)^2 \quad (J)$$

In this case the molar concentration of the monovalent Na ion is x and $y+z$, outside and inside the micellar solution, respectively while the corresponding concentration of the SO_4 ion is $\frac{x}{2}$ and $\frac{y}{2}$ and the excess ion concentration in the micellar solution becomes

$$e = 3/2 y + z - 3/2 x \quad (N)$$

Without going into further details it might be stated that the corresponding expression in the case of a trivalent anion becomes

$$e = 4/3 y + z - 4/3 x$$

and in the case of a tetravalent anion:

$$e = 5/4 y + z - 5/4 x$$

From the foregoing it is evident that the suppression of the osmotic pressure or the swelling of colloids by the addition of electrolytes is a function of the valence of both of the ions as well as of their concentration. It will be shown that this influence expresses itself in the case of soil colloids either in a difference in the value of e or in a difference in swelling. When the gel is free to swell, e remains constant, whereas if the swelling is inhibited e is increased. This can best be understood after the experimental data have been presented and will then be discussed.

THE DISTRIBUTION OF IONS IN A BENTONITE GEL

In the experiment given in table 1 the concentration of the solution outside the gel, that is, the value of x only, was determined. Since the volume of the micellar solution was unknown the value of y could not be ascertained. In the following experiments the concentration of the solutions inside and outside the gel at equilibrium has been determined. This was done in the following manner:

Graduated cylinders of 100 cc. capacity were cut off at the 60 cc. division. Twenty-five cc. of the solution to be studied were placed in each cylinder and portions of the dried granulated soil colloid or bentonite¹ were added until all of the solution was imbibed. About two days was generally allowed to complete the imbibition. A parchmentized Whatman diffusion shell was then thrust into the gel and 15 cc. of the same solution was placed inside the shell. This quantity left the level inside the shell somewhat below the level of the gel, thus creating a slight hydrostatic pressure within the gel. The latter could therefore never become flooded but was compelled to retain its water against a pressure represented by the difference in level.

The amount of liquid imbibed is not very constant but varies with the size of the granules and with the quantity added at any one time. If the granules and the quantities added are very large, partial voids may be formed within the gel, or a mass will result at the bottom of the cylinder so compact as to prevent a maximum swelling. The best results were obtained in the case of the highly swelling bentonite and the alkali-saturated soil colloids by using the granules which passed a sieve having 12 meshes to the inch but were retained by a sieve having 50 meshes. In the case of the materials saturated with the divalent cations a more homogeneous gel is formed by using more finely granulated material. The bentonite, which is not always uniform in its natural condition, was made into a thick paste and thoroughly homogenized by mixing. It was then dried at 110°C. and granulated as described.

When the colloid is allowed to swell under the conditions described in the foregoing we may look upon the liquid within the gel as belonging entirely to the micellar liquid. If the micelles with their osmotically held liquid envelopes retain their spherical form, this would not be strictly true as the interstices would then not belong to the micelles, but when the swelling takes place under restraint in a confined space with a limited amount of liquid it is probable that the micellar ions diffuse into the interstitial spaces. This is still more probable in the cases where an excess of colloid above that just needed to imbibe the 25 cc. solution was used.

The cylinders, tightly stoppered, were left to stand three days until equilibrium was established. Ten cubic centimeters were then withdrawn from the

¹ The sample of bentonite here used was the same as that previously studied by Anderson and Mattson (2). For a description and analysis of the soil colloids see authors' reference (13).

solution in the diffusion shell. The shell was then removed from the gel and about 10 gm. of the gel was rapidly placed in a crucible, provided with a lid, and weighed. The gel was then dried over night at 110°C. and again weighed. The weight of the imbibed water and of the dry colloid was thus obtained. The latter was then moistened with a normal solution of MgCl_2 or MgSO_4 , depending upon which of the anions would not interfere with the analysis. This was

TABLE 3
The Cl ion distribution in the NaCl-bentonite system

x	0.00641	0.01214	0.02830	0.05440	0.10600
y	0.00455	0.00925	0.02370	0.04840	0.09690
$x - y$	0.00186	0.00289	0.00460	0.00600	0.00910
z	0.00448	0.00668	0.01009	0.01274	0.01905
$\frac{x}{y}$	1.409	1.312	1.194	1.124	1.095
$\log \frac{x}{y}$	0.1488	0.1181	0.077	0.0507	0.0395
P.D.....	8.63	6.85	4.47	2.94	2.29
$e = 2y + z - 2x$	0.00076	0.0009	0.00089	0.00074	0.00085
water					
colloid	9.51	9.45	9.41	9.57	8.77
M. E. cations dissociated per gram...	0.0427	0.0630	0.0952	0.1212	0.1670
Per cent dissociation.....	5.35	7.88	11.88	15.17	20.90
(P.D.) z	0.0387	0.0458	0.0451	0.0374	0.0436

TABLE 4
The NO_3 ion distribution in the NaNO_3 -bentonite system

x	0.00130	0.00610	0.01190
y	0.00082	0.00430	0.00910
z	0.00124	0.00435	0.00646
$\frac{x}{y}$	1.585	1.418	1.308
$\log \frac{x}{y}$	0.2001	0.1516	0.1165
P.D.....	11.60	8.79	6.76
$e = 2y + z - 2x$	0.00028	0.00075	0.00086
water			
colloid	9.91	9.59	9.45
(P.D.) z	0.0144	0.0382	0.0436

done to prevent excessive swelling and dispersion, and to make washing possible. After that the mass was transferred to the filter and washed with a hot 0.01 N solution of the magnesium salt until the free ions in the gel were removed. The filtrate, which usually measured 250 cc., was evaporated and the anion of the solution imbibed by the gel was quantitatively determined. The concentration of this ion in the gel at equilibrium was calculated after the grams of water imbibed were converted into cc. by dividing by the density of water at the tem-

perature of the laboratory. The result was taken to represent the concentration (y) of the anion in the micellar solution. The concentration (x) of the outside solution at equilibrium was found by analysis of the 10 cc. removed from the shell. To this solution the same amount of magnesium salt was always added.

This method of determining the distribution of the ions of the free electrolyte between the gel and the outside solution is only applicable when one of the

TABLE 5
The SO_4 ion distribution in the NaSO_4 -bentonite system

x	0.01465	0.04694	0.11090
y	0.01040	0.03932	0.09840
$x-y$	0.00425	0.00762	0.01250
z	0.00699	0.01196	0.01930
$\frac{x}{y}$	1.408	1.194	1.127
$\log \frac{x}{y}$	0.1485	0.0770	0.0518
P.D.....	8.61	4.47	3.00
$e = \frac{3}{2}y + z - \frac{3}{2}x$	0.00062	0.00053	0.00055
water colloid.....	9.64	9.54	8.87
M. E. cations dissociated per gram.....	0.0673	0.1140	0.1710
Per cent dissociation.....	8.42	14.30	21.40
(P.D.) z	0.0602	0.0535	0.0578

TABLE 6
The $\text{Fe}^{+++}(\text{CN})_6$ ion distribution in the $\text{Na}_4\text{Fe}(\text{CN})_6$ -bentonite system

Original solution.....	0.01036	0.02592	0.05256	0.10748
x	0.01210	0.03056	0.05952	0.11432
y (calculated).....	0.00935	0.02250	0.04798	0.10184
$\frac{x}{y}$	1.294(?)	1.358	1.240	1.123
P.D.....	6.50(?)	7.71	5.42	2.92
water colloid.....	9.92	9.72	9.62	8.77

ions, the anion in the case of electronegative soil colloids, does not react in any way with the colloidal material. The author has previously shown that the Cl and SO_4 ions are not adsorbed by soil colloids in neutral and alkaline solutions. The same is true of the NO_3 and apparently also of the $\text{Fe}^{+++}(\text{CN})_6$ ions. The PO_4 ion is, however, adsorbed under all conditions of pH. Phosphates could therefore not be used in these experiments because, the adsorption being reversible, some of the adsorbed ions together with the free ions would be removed from the gel by the washing, giving a value for y which might be even

larger than x . In other words, the negative adsorption of the free ions, which nevertheless would exist, would be obscured by the positive adsorption.

Tables 3, 4, 5, and 6 show the concentrations of the Cl, NO₃, SO₄, and Fe⁺⁺⁺ (CN)₆ ions inside (y) and outside (x), the bentonite gel at equilibrium at varying concentrations of the respective sodium salt. The sodium salts were chosen because the sample of bentonite used was almost entirely a Na-saturated product.

One of the objects of these experiments was to determine the influence of valence upon the distribution of the ions. It was therefore thought desirable to keep the concentration of the bentonite in the gel constant. It was found that 2.5 gm. bentonite would imbibe 25 cc. of either solution up to 0.1 *N*. This quantity was therefore added to each cylinder and after imbibition the gel was homogenized by stirring with a glass rod before the diffusion shell was introduced. The differences in the $\frac{\text{water}}{\text{bentonite}}$ ratio in the gels found after equilibrium are due to osmotic readjustments with the water in the shells.

In calculating the value of z and the P.D., complete dissociation was assumed. In the case of the monovalent NO₃ and Cl ions

$$z = \frac{(x + y)(x - y)}{y} \quad (E)$$

and

$$\text{P.D.} = \frac{58}{2} \log \left(1 + \frac{z}{y} \right). \quad (G)$$

In the case of the divalent SO₄ ion

$$z = \left(\sqrt{\frac{x^2}{y}} \right) - y \quad (O)$$

and

$$\text{P.D.} = \frac{58}{3} \log \frac{(y + z)^2}{y^2}. \quad (K)$$

The P.D. may be calculated in all cases most simply independent of the valence, thus

$$\text{P.D.} = 58 \log \frac{x}{y}$$

All concentrations are in equivalents per liter and the P. D. is in millivolts.

The excess ion concentration in the gel over that of the outside solution is, in the case of the monovalent anions,

$$e = 2y + z - 2x \quad (L)$$

and in the case of the SO_4 ion

$$e = 3/2 y + z - 3/2 x$$

The tables further show the ratio of water to colloid in the gel, the milliequivalents of cations dissociated per gram bentonite, the per cent dissociation and the product (P.D.) z . The milliequivalents of cations dissociated per gram bentonite were calculated by dividing z , the average concentration of the dissociated cations in the micellar solution, by the number of grams of bentonite in 1 cc. of the gel; and the per cent dissociation is obtained by dividing the number milliequivalents dissociated per gram by 0.8, the total exchangeable cations in 1 gm., and multiplying by 100.

The experiments reveal a number of relationships of fundamental importance. Let the Cl ion distribution first be considered. The distribution of the Na ions of the NaCl or any other cations that may be displaced by the Na ions is of course the same as that of the Cl ions. x and y represent the chloride concentration outside and inside the gel respectively. Although the relative difference between x and y decreases with an increase in concentration, as shown by the values of $\frac{x}{y}$, the absolute difference between x and y increases with the concentration, amounting to 0.0091 N at a total concentration of about 0.1 N . This increase would not take place if z remained constant as one would expect it to. If anything, z might be expected to decrease because of a suppression of the dissociation by an increase in the cation concentration. On the contrary, one is surprised to find that z , as calculated from the equilibrium equation, increases with the concentration. This might lead some to doubt the applicability of the equilibrium equation to the cases here considered—but let us look a little farther. It will be seen that the P.D. decreases with the concentration and in such a way that the product of the P.D. and z is practically a constant.

How are we to account for this doubtless very significant fact? It will be shown in a later publication (part II) that the concept of ion activity becomes very useful in dealing with this problem. For the present it will be more practical to confine ourselves to the use of the term "potential." If the colloid adsorbs the base by virtue of the OH ions becoming attached to the interfacial layer of molecules, then we cannot speak of the cations as a product of ionization. Their presence in the micellar solution is merely the result of an electrostatic attraction following the adsorption of the OH ions. This adsorption of one in excess of the other of a pair of ions leads to a potential difference. This is the cataphoretic potential. Since this potential has never been found to exceed that of the common ions, it seems reasonable to assume that the adsorption of one ion in excess of the other is only possible within certain limits. The dissociated cations can remain free only below a certain potential. As the association of the OH ions with the interfacial layer proceeds further, an equiv-

alent of cations must be attracted by, and become associated with the inner layer of opposite charge; otherwise the P.D. would be much greater than is actually observed (14). If however the P.D. is reduced by the addition of an electrolyte some of the associated cations will be released, that is, the value of z will increase. This view offers an explanation why z increases with the concentration and why the product (P.D.) z is a constant.²

It is interesting to note that the excess of ions inside the gel as expressed by the difference $2y + z - 2x$ is also very nearly constant. This means that the difference in osmotic pressure between the inside of the gel and the outside solution is very nearly the same at equilibrium. We shall return to a discussion of this phenomenon in connection with later experiments.

From purely theoretical considerations based upon the electrokinetic behavior of the colloids, the author (13, 14) arrived at the conclusion that only a fraction of the exchangeable bases could exist in the dissociated condition. This conclusion is verified by these experiments as shown in the tenth row of the table. The per cent dissociated is, however, larger than it should be if we are to accept the formula (C) generally used to relate the charge of colloidal particles to the cataphoretic potential of the double layer. But since the number of free charges, that is, the number of ions dissociated, increases with an increase in concentration it is evident that this formula does not apply in its present simple form. The cataphoretic potential cannot be proportional to the number of ions dissociated but rather to their number multiplied by the activity coefficient (see part II).

In figure 1 the value of x , y , z , and e of table 3 are plotted as functions of x . If the apparently constant value of e , which equals about 0.0008 N holds for the lowest concentrations of x and y it is evident that the lower limit of $z = e = 0.0008$ when x and $y = 0$.

Turning now our attention to the distribution of the NO_3 ion we note that the figures in the last two columns of table 4 agree very closely with the corresponding figures in columns 2 and 3 in table 3. This agreement is in accordance with the Donnan equation since both ions are monovalent. The NO_3 ion was determined colorimetrically. For this reason the experiment covers only dilute solutions. In the case of the lowest concentration used (about 0.001 N) an abnormal drop in the value of z , e , and (P.D.) z will be observed. The explanation is the following. The bentonite contains a small but, in comparison to low concentrations, an appreciable quantity of sulfate. This will not affect the calculation of the P.D., which depends solely on the relative concentration of x and y , but the calculated value of z will be too low unless x and y represent absolute concentrations.

The economic significance of the negative adsorption is readily recognized in the case of the NO_3 ion. Everyone knows that nitrates are easily leached out

² A close examination of the data presented by Loeb (12, p. 186) discloses a similar behavior in the case of gelatin. This will be discussed in part II.

of the soil but the true cause of this loss has not been understood. We now see that the NO_3 ion is not only "weakly adsorbed" but negatively adsorbed inasmuch as the micellar solution constantly throws an excess of these ions into the outside solution, that is, the solution which moves by gravity and is easily lost.

This, by the way, leads us to recognize two forms of soil solution, the distinction between which is of fundamental importance. The micellar solution is an integral part of the micelle. Any attempt to remove this solution by

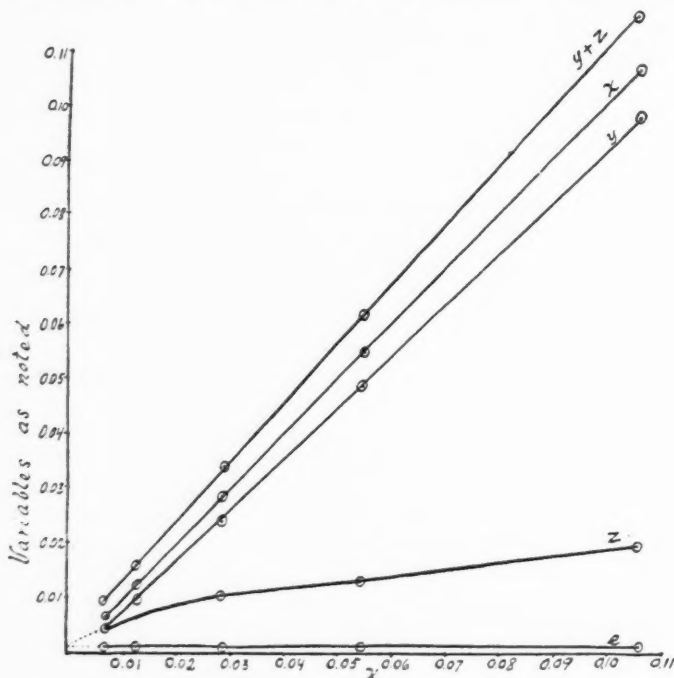


FIG. 1. THE VARIATIONS IN THE VALUES OF x , y , z AND e IN THE DONNAN DISTRIBUTION OF IONS IN A BENTONITE GEL AND IN THE OUTSIDE SOLUTION

pressure or any other means must fail. The micelle is like a living organism. It reacts to any change in the surrounding medium only more quickly because it has no membrane. Remove the water and the micelle is destroyed, leaving an inert particle comparable to the spore of an organism. This process is reversible. In dilute solutions (hypotonic) it swells; in strong solutions (hypertonic) it shrinks. It strives to maintain a definite osmotic pressure within its solution, as will be shown later. This analogy will be more evident as we proceed with our work.

As we study table 5 we observe differences in the various variables, as com-

pared to table 3 and 4, which are the direct result of the higher valence of the SO_4 anion. The value of z remains about the same at the corresponding concentrations. This is as it ought to be, considering that the $\frac{\text{water}}{\text{colloid}}$ ratio is also

nearly the same. The values of $x - y, \frac{x}{y}$, and the P.D. as compared with those of the corresponding concentrations in table 3 are very nearly as much higher as the theory demands. (Compare this with the theoretical differences in the case of mono- and divalent anions as given in the third and fourth row in table 2). The value of $e = 3/2 y + z - 3/2 x$ is again very nearly constant but is lower by about one third than this value in the case of the mono-valent ions. The product (P.D.) z is of course higher since the P.D. is higher and z is the same, but here again the constancy appears to hold.

The experiment with the ferrocyanide was not very successful. When the gel was dried, this ion was partly decomposed, as evidenced by a blue coloration. The concentration within the gel (y) was therefore calculated from the concentration in the outside solution (x) and from that in the original solution. The volumes of the respective solutions were calculated from the volume of the original solution (40 cc.), the total weight of dry colloid (2.5 gm.), and the $\frac{\text{water}}{\text{colloid}}$ ratio. The ion was determined by the oxidation method with KMnO_4 .

According to theory the P.D. values at the same concentrations of the chloride and ferrocyanide should be in the proportion of 1.0 to 1.6 (compare table 2). This relationship is only approximated by the P.D. values in the third and fourth columns in table 6. The P.D. in the second column is even lower than in the case of the Cl ion, whereas the P.D. in the fifth column is somewhat lower than in the case of the SO_4 ion at the corresponding concentrations. It is safe to assume that these discrepancies are due to errors and that the relatively higher values in columns 3 and 4 represent more nearly the actual P.D.

The suppression of the P.D. ($= 58 \log \frac{x}{y}$) by the chloride, sulfate, and ferrocyanide of sodium is graphically represented in figure 2.

THE RELATION BETWEEN VALENCE AND SWELLING

In the last chapter we saw that the valence effect of the anions on the distribution of the electrolyte between the gel of an electronegative colloid and the outside solution expresses itself in such a way that the higher the valence the greater the difference between x and y . It will be recalled that in the above experiments the concentration of the colloid in the gel was about the same in all cases, the gels being prepared by allowing 2.5 gm. dry colloid to imbibe 25 cc. of the different solutions.

In continuing these experiments by employing still stronger solutions it was found that 2.5 gm. bentonite were no longer sufficient to imbibe the 25 cc. of the solutions and that the power of imbibition decreased more rapidly in the

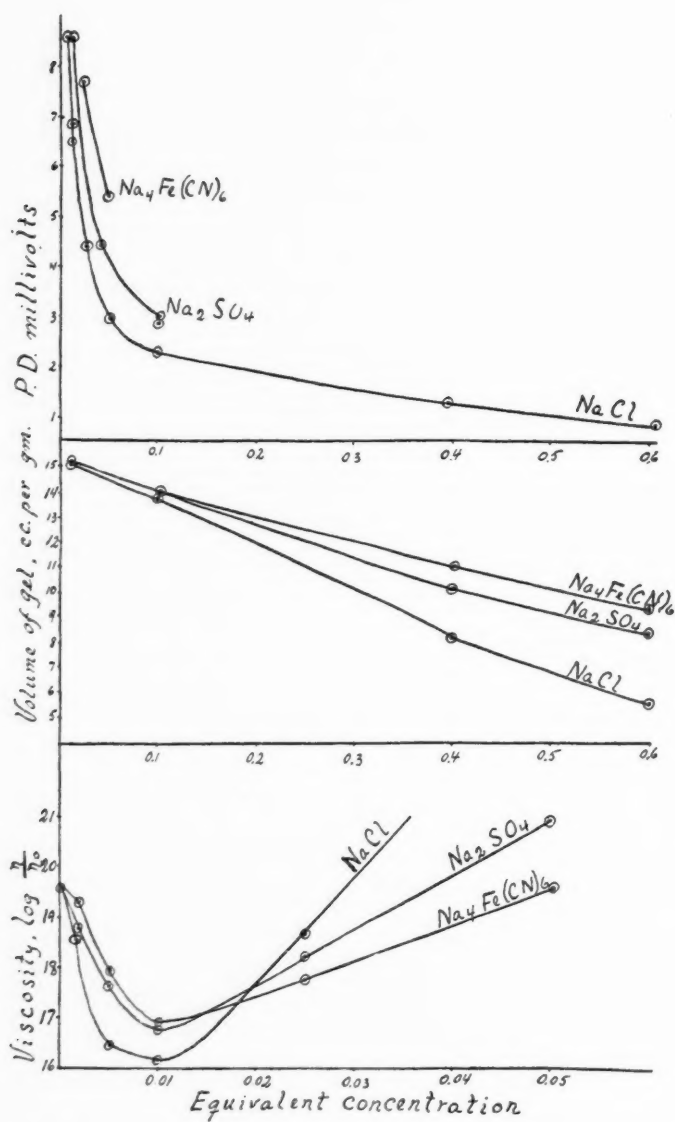


FIG. 2. THE INFLUENCE OF THE VALENCE OF THE ANION ON THE SUPPRESSION OF THE P.D., THE SWELLING, AND THE VISCOSITY OF BENTONITE

chloride than in the sulfate solution and in the sulfate solution more rapidly than in the ferrocyanide solution. These differences became very marked at concentrations about 0.4 to 0.6 *N*. The experiments were therefore conducted in such a way that additional small quantities of bentonite were gradually added to each cylinder until all of the 25 cc. was imbibed. The method is not very accurate but the resulting gels represented roughly a saturated condition. The diffusion shells were then inserted and filled with 15 cc. of the respective solutions. The distribution at equilibrium is given in table 7.

The most significant fact revealed by these experiments is that here the valence effect expresses itself, not in a difference in the values of $\frac{x}{y}$ and in a difference in P.D., as is the case when the concentration of the gel is kept constant, but chiefly in a difference in swelling as shown by the $\frac{\text{water}}{\text{colloid}}$ ratio.

TABLE 7
Distribution of the Cl, SO₄, and Fe⁺⁺⁺ (CN)₆ ions and the relation between valence and swelling

	NaCl		Na ₂ SO ₄		Na ₄ Fe(CN) ₆
<i>x</i>	0.4160	0.6256	0.4090	0.6110	0.4120
<i>y</i>	0.3960	0.6050	0.3894	0.5864	0.3920
<i>x</i> - <i>y</i>	0.0200	0.0206	0.0196	0.0246	0.0200
<i>z</i>	0.0410	0.0419	0.0298	0.0373
$\frac{x}{y}$	1.050	1.034	1.050	1.042	1.051
P.D.....	1.25	0.84	1.23	1.03	1.25
<i>e</i>	0.0010	0.0007	0.0004	0.0004
$\frac{\text{water}}{\text{colloid}}$	4.72	3.06	7.25	6.18	7.68
(P.D.) <i>z</i>	0.0512	0.0352	0.0366	0.0384

This is especially true in the case of the 0.4 *N* solutions. Here the values $x - y$, $\frac{x}{y}$, and the P.D. are almost identical, while the $\frac{\text{water}}{\text{colloid}}$ ratio bears the relation of 1.00, 1.33, and 1.42 in the case of the chloride, sulfate, and ferrocyanide respectively.

Since imbibition dilutes the micellar solution it is obvious that *z* must decrease as the swelling increases. The value of *z* is accordingly lower in the sulfate than in the chloride gel, the difference being such as to yield a more nearly uniform distribution ratio and P.D.

It appears that the swelling is markedly suppressed only at a concentration above 0.1 *N* whereas the P.D. is greatly affected in much lower concentrations. It seems, therefore, that the electrostatic stress is the one first to be undone by the effect of the electrolyte. After the P.D. has been considerably reduced the suppressing effect is transferred to the swelling. The latter, i.e.,

the imbibition, adjusts itself apparently in such a way as to keep the osmotic pressure, i.e., the value of e , constant.

The results of the above work may be summarized in the following statements:

When the concentration of the colloid in the gel is constant, that is, when the swelling is inhibited, the valence effect expresses itself in differences in the P.D.

When the gel is permitted to swell to a maximum the valence effect expresses itself in differences in the degree of swelling, i.e. in the quantities of water imbibed. It might be said that the gels tend to swell to the same P.D. in the same concentrations of the various salts.

TABLE 8
Effect of an interchange in colloid concentration on the distribution of Cl and SO₄ ions

	NaCl				Na ₂ SO ₄			
	A		B		A		B	
Bentonite grams in 25 cc.....	5.7	5.7	3.1	3.1	3.1	3.1	5.7	5.7
x	0.5222	0.5217	0.5132	0.5138	0.5136	0.5138	0.5310	0.5306
y	0.4941	0.4935	0.4953	0.4982	0.4849	0.4845	0.4745	0.4711
$x - y$	0.0281	0.0282	0.0179	0.0156	0.0287	0.0293	0.0565	0.0595
z	0.0580		0.0340		0.0441		0.0895	
$\frac{x}{y}$	1.057		1.034		1.059		1.122	
P.D.....	1.40		0.83		1.45		2.91	
e	0.0016		0.0006		0.0006		0.0025	
water								
colloid	3.27		5.98		6.06		3.60	

When a system is at equilibrium and no work is done on the system, certain functions and the total free energy must be at a minimum. If the osmotic pressure alone governed the swelling the gel would swell indefinitely until $e = 0$. But since the osmotic pressure is opposed by an electrostatic attraction on the dissociated ions an equilibrium is established at a point where the osmotic pressure has been reduced to between 0.01 or 0.02 atmosphere.

(The osmotic pressure = $22.4 \times \frac{273 + t^\circ}{273} \times e$ atmospheres.) If the gel is

compressed or if it is prevented from swelling, both the P.D. and e will increase because of an increase in the value of z . The value of e will not increase, however, in proportion to the compression, because of the compensating effect of the Donnan distribution. Following the law of Le Chatelier and Braun the equilibrium of the system will be displaced in that direction which tends to undo the stress brought to bear upon it. When the gel is compressed the osmotic stress is kept down by forcing ions into the outside solution. But

this creates a higher P.D. and therefore an opposing stress. When the gel is free to swell, both the osmotic and the potential stresses attain a minimum through the imbibition of water.

This is shown more clearly by the following duplicated experiments. It was found by gradually adding bentonite to approximately 0.5 *N* NaCl and Na₂SO₄ solutions that 5.7 gm. of the dry substance was required to imbibe 25 cc. of the chloride, whereas 3.1 gm. sufficed to imbibe 25 cc. of the sulfate solution. In a duplicate series of cylinders the quantity of bentonite required to imbibe the chloride solution (5.7 gm.) was added to the sulfate solution, whereas the quantity required to imbibe 25 cc. of the sulfate solution (3.1 gm.) was added to the chloride solution. In the second series, the sulfate gel represents, therefore, a compressed gel whereas the chloride gel contained more liquid than would normally be imbibed. The gels were homogenized with a glass rod before the diffusion shells containing the respective solutions were introduced. The equilibrium distribution is shown in table 8.

In comparing the two A columns, which represent the conditions of equilibrium after free imbibition, we observe in a general way the same relationship

TABLE 9

Distribution of the Cl and SO₄ ions at the same $\frac{\text{water}}{\text{colloid}}$ ratio

	<i>x</i>	<i>y</i>	<i>x - y</i>	<i>z</i>	P.D.	<i>e</i>	$\frac{\text{WATER}}{\text{COLLOID}}$
NaCl.....	0.4091	0.3870	0.0221	0.0455	1.40	0.0013	7.41
Na ₂ SO ₄	0.4210	0.3895	0.0315	0.0481	1.96	0.0009	7.15

as in table 7. The swelling is very much greater in the case of the sulfate-treated gel. The greater swelling of this gel has reduced the value of *z* to such an extent that the difference between *x* and *y*, which directly depends upon *z*, is very nearly the same as in the chloride gel. The swelling has reduced the P.D. to the same value in both gels.

The figures in the B columns, representing dilution of the gel on the one hand and compression on the other, are very different. The results in the chloride (B) column are really not significant. All the figures are lower than in the chloride (A) column. This is to be ascribed to the presence of "outside" solution within the gel, *y* representing therefore not merely the micellar concentration but a mixture of *x* and *y*. The figures in the sulfate (B) column show a pronounced increase as the $\frac{\text{water}}{\text{colloid}}$ ratio was decreased from 6.06 to 3.60. The values of *x - y*, *z*, and the P.D. are about twice as high as in the A column, whereas *e* is four times greater.

In order to show the effect of the valence of the anions in higher concentrations when the ratio $\frac{\text{water}}{\text{colloid}}$ is constant, the experiment was modified as follows:

Two and a half grams of bentonite were allowed to imbibe 25 cc. distilled water, and the diffusion shells were put in place and filled with 15 cc. normal chloride and sulfate solutions. Because of the fact that all of the electrolyte was on one side of the membrane at the outset, 10 days were allowed for equilibrium. The results are shown in table 9.

These experiments leave no doubt that the valence of the ion of the same sign of charge as that of the colloid is a factor influencing the distribution of the ions and the suppression of the swelling. In the last experiment where the $\frac{\text{water}}{\text{colloid}}$ ratio differed only slightly, the difference between x and y (and the calculated P.D.) in the case of the two salts correspond fairly well with the difference demanded by the equilibrium equation, considering the analytical difficulties. It should be stated that the assumption of complete dissociation does not seriously affect the relative values in the case of the different salts at the same concentrations. The salts are ionized to about the same extent and the undissociated molecules distribute themselves equally throughout the

TABLE 10
Distribution of Cl and SO₄ ions within the same gel

	x	y	$x - y$	$\frac{x}{y}$	P.D.	$\frac{\text{WATER}}{\text{COLLOID}}$
NaCl (A).....	0.2677	0.2464	0.0113	1.0457	5.74
NaCl (B).....	0.2580	0.2468	0.0112	1.0454	1.12	5.80
Na ₂ SO ₄ (A).....	0.2606	0.2489	0.0117	1.0470	5.74
Na ₂ SO ₄ (B).....	0.2606	0.2494	0.0112	1.0450	1.13	5.80

system. The absolute difference between x and y as found by analysis is independent of the degree of ionization. The calculation of z is therefore unaffected, but the P.D., which depends upon the relative magnitudes of x and y , will in reality be higher than the calculated value.

Since the ions distribute themselves between the gel and the outside solution according to valence it seemed of interest to determine how this effect would express itself when ions of different valence are added to the same gel. For this purpose 0.5N NaCl and Na₂SO₄ solutions were mixed in equal proportions, making the solution $0.25 \frac{N}{4}$ with respect to each salt. The experiment was carried out in duplicate, the results of which are shown in table 10.

The experiment in itself shows no apparent valence effect. The difference between x and y is the same within the limits of error, in the case of both ions. A comparison with table 8 (NaCl, B column, and Na₂SO₄, A column) will show however that the foregoing values of $\frac{x}{y}$ and of the $\frac{\text{water}}{\text{colloid}}$ ratio are all intermediate between the values obtained with NaCl and Na₂SO₄ separately

at the same concentration. In the last experiment there can only be one P.D. and one degree of imbibition for both electrolytes since both were present in the same system. The result represents therefore the algebraic sum of the action of both.

THE EFFECT OF THE HYDRATION OF IONS ON THE DONNAN DISTRIBUTION AND ON THE SWELLING

In a series of interesting experiments Wiegner (23) has shown that the addition of alcohol increases the power of the alkali cations to displace the divalent cations from the soil complex. Wiegner ascribes this effect to a dehydration of the otherwise heavily hydrated alkali cations. When freed from their water envelope the small alkali cations show a greatly increased displacing power. This increased displacing power simply means that the dehydrated ions are more strongly attracted by the inner layer of opposite sign of charge,

TABLE 11
The effect of alcohol on the distribution of the Cl ion in the LiCl-bentonite system

Cc. 95 per cent alcohol in 100 cc.....	20	40	60	80
x	0.01548	0.01535	0.01490	Lost
y	0.01189	0.01230	0.01326
$x - y$	0.00359	0.00305	0.00164
z	0.00826	0.00686	0.00348
$\frac{x}{y}$	1.300	1.248	1.124
P.D.....	6.61	5.58	2.94
e	0.00108	0.00076	0.00020
water				
colloid.....	6.40	5.68	4.78	1.24
Per cent dissociation.....	6.62	4.87	2.07

that the tendency of the dehydrated ions to remain dissociated in the micellar atmosphere has been lessened. Association at the interface takes the place of the association with the water molecules. The dehydrated ion is unstable, it cannot exist alone, its potential being too high.

This being the case, the effect of dehydration should show itself in the Donnan distribution, for if z is decreased because of a lessened dissociation the difference between x and y will be smaller. Also, the swelling should for the same reason decrease, apart from any direct dehydrating effect upon the colloid.

In the following experiment increasing quantities of alcohol were added to the solutions, LiCl being used instead of NaCl because of its greater solubility. (See table 11.)

The results of the experiment show the predictions to be fulfilled. The values of z , and therefore also $x - y$, $\frac{x}{y}$, and the P.D. decrease as the percentage of alcohol is increased, that is, as the cations are dehydrated. The percentage

of the exchangeable cations dissociated was calculated as described in the foregoing and shows a corresponding decrease. The quantity of water imbibed, i.e., the swelling, falls off very rapidly above 60 per cent alcohol. In this connection it may be added that 70 per cent alcohol flocculated a bentonite suspension completely without any electrolyte.

THE EFFECT OF COLLOID CONCENTRATION ON THE ION DISTRIBUTION IN THE Na_2SO_4 BENTONITE SYSTEM

In the following experiment the concentration of Na_2SO_4 was the same in all cases while the quantity of bentonite was increased from 2.5 to 3.5 gm. in each 25 cc. of the solution. The colloid concentration could not be carried beyond this point as the gel then became too stiff. (See table 12.)

Since a maximum swelling was prevented in all cases the effect of the variations in the concentration of the colloid shows itself in differences in the other

TABLE 12
The effect of colloid concentration

Gm. bentonite in 25 cc.....	2.5	3.0	3.5
x	0.01448	0.01542	0.01559
y	0.01033	0.01041	0.00985
$x - y$	0.00415	0.00501	0.00574
z	0.00681	0.00836	0.01035
P.D.....	8.49	9.89	11.57
e	0.00058	0.00084	0.00174
$\frac{\text{water}}{\text{colloid}}$	9.83	8.10	7.42
$\frac{r_1}{r}$	2.990	2.814	2.737

variables. The values of z , $x - y$, P.D., and e all increase with the decrease in the $\frac{\text{water}}{\text{colloid}}$ ratio. Since the sulfate concentration is constant, the value of z is the sole factor upon which all relationships hinge.

THE MICELLAR STRUCTURE

From the different values of z as calculated from the results of this experiment it will be possible to gain some information as to the distribution of the micellar cations in the micellar atmosphere. The magnitude of z as measured in the gel as a whole depends upon the number of micelles per unit volume and upon the average micellar ion concentration within the individual micelles. Since the three gels in the foregoing experiment all contained less water than would be freely imbibed osmotically, it is safe to assume that the micelles occupy a closely packed position and that all the liquid within the gels represents micellar liquid. Now since the quantity of liquid permitted to be imbibed was different in the case of each gel it follows that the thickness of the micellar

atmosphere differed accordingly, being thickest in the least concentrated gel and thinnest in the most concentrated gel. Although the size of the colloidal particles is unknown the relationship between the average radius r of the particles and the radius r_1 of the micelles may be calculated from the $\frac{\text{water}}{\text{colloid}}$

ratio, a specific gravity of 2.65 being assumed for bentonite. The $\frac{r_1}{r}$ ratios thus found for the three gels are given in table 12. Since $r_1 = r + \text{thickness of the micellar atmosphere}$, this thickness is $1.99 r$, $1.814 r$, and $1.737 r$, respectively. The corresponding z values are 0.00681, 0.00836, and 0.01035. These figures represent, of course, the average concentrations within the micellar atmosphere of thickness $r_1 - r$ and not the concentration at any one point.

It is evident that the concentration or ion density in the micellar atmosphere decreases rapidly with the "height," i.e., the distance from the surface of the particle. Near the surface the concentration must be very high whereas in the outermost strata of the atmosphere the density approaches zero at the point of maximum imbibition. The same statement applies to the P.D. between the interior of the atmosphere and the outside solution. This P.D. must increase with the depth of the atmosphere, being greatest near the surface of the particle. The P.D. as calculated from the free ion distribution represents therefore, only the average P.D. for the gel as a whole. Within the micelle, y will decrease as z increases, hence the calculated P.D. will grow larger with the concentration of the gel. This explains why the P.D. between the gel and the outside solution does not exceed 12 millivolts even in the most concentrated gel while the cataphoretic potential may be several times greater. It seems probable that the limiting value for the foregoing P.D. (the Donnan potential) should bear a definite relationship to the cataphoretic potential but this will be discussed more profitably in connection with cataphoresis.

From the preceding $\frac{r_1}{r}$ ratios and from the corresponding z values, it would be possible to calculate the variation in ion density with the height in the micellar atmosphere, but because of the very narrow interval covered by the $\frac{r_1}{r}$ ratios, any error in the z values would be so magnified as to render such computations worthless. The foregoing experiments and calculations make it quite evident that the outer Helmholtz layer is not only diffuse, as first pointed out by Gouy (9), but that the ion density decreases in some inverse proportion to the distance from the particle.

THE BEHAVIOR OF ELECTRODIALYSED BENTONITE AT VARIOUS DEGREES OF SATURATION WITH NaOH

In the preceding experiments only the natural untreated bentonite was used. For the following experiment the bentonite was electrodialyzed until all the exchangeable bases were removed. The exchange capacity of the original

material was 0.803 milliequivalents per gram. Subsamples of the electro-dialyzed sample were saturated to the extent of 0.2, 0.4, 0.6, and 0.8 milliequivalents of NaOH per gram. Portions of the granulated materials were gradually added, each to 25 cc. of a Na_2SO_4 solution, until all of the liquid was imbibed. The experiment with the diffusion shells was then continued, as has been described. The series was extended, however, to include four cylinders to which an excess of NaOH was added. Since the major portion of it would remain unadsorbed, the excess base was added to the sulfate solutions to which bentonite, saturated to the extent of 0.8 milliequivalents per gram, was added, as before in quantities sufficient to imbibe the 25 cc. After equilibrium was established the sulfate concentration was determined inside (y) and outside (x) the gel. The results are given in table 13.

TABLE 13

The SO_4 ion distribution in electro-dialyzed bentonite saturated with various quantities of NaOH

M.Eq. NaOH per gram...	0.0	0.2	0.4	0.6	0.8	0.8	0.8	0.8	0.8
Excess NaOH in Na_2SO_4 solution....						1.0	2.0	4.0	20.0
x	0.01435	0.01409	0.01336	0.01396	0.01439	0.01375	0.01413	0.01353	0.01401
y	0.01203	0.01091	0.01030	0.01063	0.01053	0.01096	0.01131	0.01143	0.01341
$\frac{x}{y}$	1.193	1.290	1.300	1.313	1.366	1.255	1.249	1.184	1.045
z	0.00364	0.00509	0.00492	0.00537	0.00629	Not determinable			
P.D.	4.44	6.41	6.61	6.86	7.85	5.72	5.60	4.26	1.11
e	0.00016	0.00032	0.00033	0.00037	0.00050				
water colloid.....	2.99	4.07	7.94	8.74	8.90	8.38	6.98	6.48	2.76
Per cent cations dissociated.	1.35	2.59	4.88	5.88	7.00				

The most significant fact revealed by this experiment is the existence of points of maxima with respect to the value of $\frac{x}{y}$ and the P.D. as well as to the quantity of water imbibed and that these maxima coincide with the quantity of NaOH corresponding to the base exchange capacity or 0.8 milliequivalents per gram. This relationship is not surprising and could even be predicted on the basis of the author's earlier work (15).

The results, graphically represented in figure 3, are to be interpreted as follows: In the electro-dialyzed material the cations in the micellar atmosphere are H ions except for some exchange with the Na ions of the added sulfate. The H ion, with its single molecule of water with which it is supposed to associate, is very small and possesses, accordingly, a high potential. It responds readily, therefore, to the electrostatic attraction of the inner layer. The result

is a low ion concentration in the micellar atmosphere, a low P.D., a low osmotic pressure, and a low imbibition. As the H ions are displaced by the Na ions there is an increase in the micellar ion concentration, the P.D. is increased, and the bentonite gradually regains its original power to swell, which attains a maximum at the neutral point. This explains the ascending part of the curves representing the P.D., the swelling and, as we shall see later, also the viscosity.

On the alkaline side of the neutral point the colloid continues to adsorb some of the base but the augmenting effect of this on the P.D., the osmotic pressure, and the swelling is more than offset by the suppressing effect of the free base. The excess, or free base, acts exactly as any other added electrolyte, hence the descending path of the curves.

The suppressing effect in this experiment was entirely due to the excess base and not to the added sulfate, which was kept constant except for fluctuations due to impurities. The sulfate was merely added as a convenient method of determining the equilibrium ratio $\frac{x}{y}$.

The determination of the concentration of any anion inside and outside the gel at equilibrium must give the same value for $\frac{x}{y}$. If the anion enters into combination with the colloid then the method here used of removing the free anions from the gel by washing is of course not applicable, since then some of the combined anions would also be removed. The OH ions could therefore only be determined in situ without disturbing the equilibrium, as with the hydrogen electrode. The equilibrium ratio would also be expressed by the hydrogen-ion concentrations inside and outside the gel. In the case of the electronegative colloid the cation concentration is greater inside the gel than in the outside solution, the concentration inside the gel being $y + z$, whereas in the outside solution it is x . The foregoing ratio would therefore be expressed by

$$\frac{(\text{H}^+) \text{ inside}}{(\text{H}^+) \text{ outside}} = \frac{y + z}{x}.$$

This equals $\frac{x}{y}$, as has been shown. Since

$$\text{pH inside} = -\log (y + z)$$

and

$$\text{pH outside} = -\log x$$

$$\log \frac{y + z}{x} = \text{pH outside minus pH inside.}$$

The use of the hydrogen electrode was however precluded because of the solidity of the gels. In systems of greater fluidity the method has been used with the result that a higher hydrogen-ion concentration was invariably found within the electronegative suspension than in the outside solution in equilibrium with the suspension. In the case of soil colloids high in sesquioxides which become electropositive in acid solutions the hydrogen-ion concentration is higher in the outside solution.

In the preceding experiment the value of z could be calculated from the sulfate-ion distribution only in the cases where the sulfate was the only free electrolyte present. The relative concentration of the free hydroxide inside and outside the gel must be the same as that of the sulfate, that is, the value of $\frac{x}{y}$ is the same for both, but in calculating z the absolute concentrations must be known.

THE INFLUENCE OF THE NATURE OF THE EXCHANGEABLE CATION AND OF THE COMPOSITION OF THE COLLOID

In the previous experiments bentonite was exclusively used because it lends itself admirably in its natural condition to investigations of the nature here dealt with, is easily obtained, and saves the laborious preparation necessary in the case of soil colloids. In its colloidal behavior bentonite resembles closely the soil colloids having the same ratio of silica to sesquioxides.

In the following experiment it was thought desirable to employ soil colloids in order to meet the possible objection that what applies to bentonite may not apply to soil colloids and also to show the influence of a difference in the silica sesquioxide ratio. The Sharkey and the Norfolk soil colloids, which have been extensively used in experiments previously reported, were accordingly selected.

The Li-, Na-, and K-saturated colloids were prepared by saturating the electrodialyzed materials with the respective hydroxides, whereas it was more convenient to prepare the Mg-, Ca-, and Ba-saturated materials by the neutral salt treatment.

The experiment was carried out by adding small portions of the granulated colloids to 25 cc. of the respective chloride solutions until all of the liquid was imbibed. The diffusion shells were then thrust into the gels and filled with 15 cc. of the chloride solution. The Cl-ion concentration in the gel and in the outside solution at equilibrium was determined gravimetrically. The results are shown in table 14.

In spite of a great deal of painstaking work the results of the experiment are not so conclusive as might be desired but, considering the difficulties encountered, a better relationship could hardly be anticipated by a repetition of the work. The results are nevertheless in a general way in agreement with the theory and even in the case of certain discrepancies, as in those of the K-saturated gel, there is something that should not be overlooked.

The alkali-saturated colloids, especially those which, like the Sharkey, contain a little humus, shrink upon drying into an extremely hard, compact mass. The humus, which does not readily return to the colloidal condition, seems to cement the particles together so that a comparatively strong osmotic force is required to overcome the cohesive force and thus again unlock the aggregates. This osmotic force was strong enough in the case of the more highly dissociated Li- and Na-saturated colloids, which readily imbibed the water, forming voluminous gels. The K-saturated gel showed, however, no tendency whatever to swell, as is shown by the $\frac{\text{water}}{\text{colloid}}$ ratio, which is about equal to that of the Ba-saturated material. When not previously dried, the

TABLE 14
The influence of the exchangeable cation and of the composition of the soil colloids

MATERIAL	SHARKEY:						NORFOLK:
	Li	Na	K	Mg	Ca	Ba	Na
Exchangeable cation.....							
<i>x</i>	0.01513	0.01276	0.01206	0.01102	0.01084	0.01088	0.01164
<i>y</i>	0.01192	0.01053	0.00786	0.00849	0.00877	0.00952	0.00875
<i>z</i>	0.00728	0.00493	0.01064	0.01007	0.00779	0.00469	0.00673
<i>x</i>							
<i>y</i>	1.27	1.21	1.53	1.30	1.24	1.14	1.33
P.D.....	6.02	4.81	10.72	6.61	5.33	3.36	7.18
<i>e</i>	0.00086	0.00047	0.00224	0.00124	0.00079	0.00031	0.00095
$\frac{\text{water}}{\text{colloid}}$	6.83	5.17	1.36	1.59	1.45	1.33	1.61
M.Eq. dissociated per gram....	0.0499	0.0256	0.0145	0.0160	0.0113	0.0062	0.0108
Per cent dissociation.....	6.25	3.20	1.81	2.00	1.41	0.78	5.15
				$\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3}$		EXCHANGE CAPACITY MILLIEQUIV./GRAM	
Sharkey.....				3.18		0.796	
Norfolk.....				1.63		0.207	

K-saturated gel swells considerably. Bentonite saturated with potassium swells considerably even after being dried (15). This material contains no protective colloid like humus and does not become so compact when dried as do the soil colloids. The aggregates are therefore more easily unlocked by the osmotic forces. It is interesting to note that the failure of the K-gel to swell shows itself in a high micellar ion concentration (*z*), in a high P.D., and in a high osmotic pressure (*e*) as compared to the gels saturated with the other monovalent cations. The per cent dissociation, however, is lowest in the K-gel, which is in agreement with the hydration theory of Wiegner and with the energy of displacement as found by Gedroiz. The order of hydration and dissociation is: Li > Na > K, whereas the order of the flocculating and displacing power is the reverse.

When comparing the action of the divalent cations with that of the monovalent, reference should be made to formulas (E), (G), and (H) and to the second and third row in table 2. In the case of the divalent cations

$$z = \frac{x^2}{y^2} - y$$

It will be noted that the values of z , the P.D., and e fall off rapidly with an increase in the atomic weight of the divalent metals. This is not in harmony with the aforemade observation that the gels strive to adjust themselves, within certain limits, to the same potential by swelling or shrinking when free to do so. If the Bagel were more concentrated all the preceding values would be greater. Since the $\frac{\text{water}}{\text{colloid}}$ ratios do not differ very much in the case of the three gels we may conclude that we are here approaching a limiting value in gel concentration. It is evident that if the osmotically imbibed water is less than the volume of the capillaries, the volume of the gel is no longer affected by the osmotic forces. In a crude way the case is analogous to van der Vaal's correction of the gas formula. When dealing with the phenomena of swelling we must take into account the irreducible volume occupied by the dispersed phase and of the interstices. The apparent swelling, especially in the case of the Ba gel must therefore be appreciably greater than the true volume of osmotic imbibition, a fact which considerably distorts the relationships.

The per cent divalent cations dissociated is again in the order of the atomic weight.



This is again the order of the lyotropic series and is the reverse of the order of the displacing power as found by Gedroiz. It is evident that the least dissociated cation must form the most stable complex.

The influence of the composition of the colloid, that is, the ratio of silica to sesquioxides, shows itself by comparing the equilibrium condition of the Norfolk to that of the Sharkey colloid. The former, with a composition ratio of 1.63, has an exchange capacity only about one-fourth that of the latter, in which the composition ratio is 3.18. The number of cations dissociated per gram of the Norfolk colloid is therefore less than in the case of the Sharkey. The result is that the Norfolk gel attains an equilibrium distribution with less imbibition, i.e. with less swelling than is required by the Sharkey gel. At the same concentrations of the Na saturated Norfolk and Sharkey gels, that is, under conditions of inhibited swelling, the negative adsorption, i.e. the value of $\frac{x}{y}$, would be considerably greater in the case of the Sharkey, whereas under conditions of free imbibition the effect of the greater ion content of the Sharkey shows itself chiefly in the form of a difference in swelling.

The valence effect, it will be recalled, expresses itself in the same way. At a constant gel concentration, the SO_4 ion gave rise to a greater $\frac{x}{y}$ ratio than the Cl ion, whereas under conditions of free imbibition the valence effect showed itself in a greater swelling of the sulfate-treated gel. The valence effect of the cations follows the same rule but is, as the theory demands, reversed, the suppressing effect of the divalent cations being greater than that of the monovalent. The suppressing effect of the cations, i.e. the ions in combination with the electronegative colloid, is twofold however. In the first place there is the effect of the degree of dissociation, which varies with each cation, giving rise to the well-known and unrefuted Hofmeister series, or the so-called lyotropic

TABLE 15
Effect of valence and concentration on the viscosity of a bentonite suspension
Relative viscosity (water = 1)

	CONCENTRATION							
	0.0 N	0.000167 N	0.005 N	0.01 N	0.025 N	0.05 N	0.1 N	0.167 N
NaCl.....	1.57	1.53	1.46	1.45	1.54	1.85	2.36	2.70
Na_2SO_4	1.57	1.54	1.50	1.47	1.52	1.62	1.77	1.81
$\text{Na}_4\text{Fe}(\text{CN})_6$	1.57	1.56	1.51	1.48	1.51	1.57	1.64	1.69

TABLE 16
The effect of NaOH on the viscosity of electrodialysed bentonite

NaOH m.equiv. per gram.....	0.0	0.2	0.4	0.6	0.7	0.8
Relative viscosity.....	1.08	1.14	1.28	1.29	1.29	1.24
NaOH m. equiv. per gram.....	0.9	1.0	1.2	1.6	2.0	2.4
				∞	∞	∞
Relative viscosity.....	1.23	1.21	1.19	1.18	1.20	1.76

series of ions. In the second place there is the effect of the Donnan distribution which is purely a valence effect.

The preceding experiment with different cations was, as already explained, not very successful, but allowing for the inherent discrepancies discussed and for the unavoidable errors in removing so small quantities of electrolyte from large volumes of gel, the results agree in a general way with the theory.

VISCOSITY

The viscosity of bentonite suspensions was determined by the use of an instrument similar in construction to the Ostwald viscometer. The time of outflow of distilled water at room temperature was 23 seconds. In one experiment the time of outflow of 5.52 per cent suspensions of untreated bentonite was determined in the presence of varying concentrations of the chloride, sulfate, and ferrocyanide of sodium. In another experiment the time of

outflow of 5.36 per cent suspensions of electrolyzed bentonite to which varying quantities of NaOH had been added was determined. The suspensions were prepared from more concentrated stock suspensions as follows:

The quantity of the stock suspensions which would be delivered from a 25-cc. pipette within a fixed time allowed for drainage was separately determined. This quantity was then placed in a series of test tubes to which the calculated amount of electrolyte was now added, making a total volume of 30 cc. The tubes were then shaken and the measurements made. The results,

as expressed in the terms of relative viscosity $\frac{\eta}{\eta_0}$ (water = 1), are given in tables 15 and 16.

The experiment with the three-salt solutions shows a suppressing effect up to a concentration of 0.01 *N*. At concentrations of 0.025 *N* and above the viscosity increases again rapidly. This phenomenon is easily explained. According to the theory of Einstein (7) and of Arrhenius (3), the viscosity is a function of the relative volume occupied by the solute (or colloid). It has been shown by Loeb (12) that the viscosity of protein solutions fits the theory in a general way.

If this relationship holds for soil colloids as well, it follows that the volume occupied by the bentonite is smaller in a 0.01 *N* solution than in less concentrated solutions. This assumption is quite justified on the basis of the preceding data on swelling. The swelling of the gel must be a direct expression of the volume of the individual micelles. The suppression of the swelling with an increase in concentration is an effect of a shrinkage in the volume of the micelles due to a decrease in the osmotic pressure, brought about by the Donnan equilibrium.

This theory is further supported by the effect of the different salts. The viscosity suffers the greatest suppression in the presence of the chloride, whereas the suppression is least in the presence of the ferrocyanide, the effect of the sulfate being intermediate. This is the same valence effect encountered in the swelling of the gels and in the Donnan equilibrium.

It remains to explain the increase in viscosity at and above a concentration of 0.025 *N*. At very high concentrations (not shown in table 15) the suspensions set into a gel. That this increase in viscosity is the direct result of aggregation is evident from the fact that the concentrations at which the increase commences coincide with the concentrations sufficient to flocculate the suspension. It will be noted that the chloride causes a more rapid increase in the viscosity than the sulfate and the sulfate a more rapid increase than the ferrocyanide, the differences being more marked in the higher concentrations. It will be shown (part II) that this represents the order in which the three electrolytes cause the suspension to flocculate. The increase in the viscosity in higher concentrations must therefore be ascribed to the impeding effect of the micellar aggregates upon the flow of the liquid. Were it not for this aggregation the viscosity would continue to decrease with an increase in the

concentration just as the volume of the individual micelles decreases, as shown by the swelling.

Directing our attention to table 16 we meet with another turning point in that we find two minima and to maxima in the viscosity. We will at once perceive a parallelism between the viscosity in this experiment and the ion distribution and the swelling in the experiment with electrodialyzed bentonite as given in table 13. In the latter experiment the second maxima is, however, absent.

Keeping in mind the theory of the soil colloid micelle propounded in the foregoing, the phenomena are easily accounted for. The electrodialyzed micelle contains only H ions in the micellar atmosphere. The concentration of this ion is smaller than that of the Na ion. The equilibrium between the opposing forces, i.e. the osmotic and the electrostatic is attained with less imbibition than in the case of the Na-saturated micelles. The micelles occupy therefore a relatively smaller volume in the electrodialyzed condition, resulting in a low viscosity. As the material is progressively saturated with NaOH the micellar ion concentration is increased, more liquid is imbibed and the volume of micelles becomes greater, which expresses itself in the form of a greater viscosity. The viscosity reaches a maximum at the proportion of 0.6 milliequivalents NaOH per gram colloid, which is somewhat less than the base exchange capacity.

With an excess of NaOH there is a drop in the viscosity as in the preceding experiments with the different salts. This is of course due to the suppressing effect of the free electrolyte, as has been explained.

In the proportion of 1.6 milliequivalents NaOH, or more, per gram bentonite the suspensions set into a gel, the relative viscosity approaching infinity as indicated in the table. When shaken vigorously the gels became temporarily quite fluid and could be run through the viscometer. The results of these measurements are shown beneath the infinity signs. This phenomenon is evidently an expression of the time required in the process of aggregation.

PLASTICITY

As the colloid concentration of a suspension is increased the viscosity increases gradually until at a certain concentration, depending upon the composition of the colloid and the nature of the exchangeable cation, a sudden great increase in viscosity is observed. The viscous flow as measured by the viscometer becomes all at once infinitely slow. This break in the viscosity curve marks the transition from a viscous to a plastic condition. The abruptness of this transition may be readily visualized. As long as the micelles can freely move about in the suspension medium, fluidity is maintained and the suspension obeys the law of liquids. When the micelles become so numerous that they occupy all the space and are in actual contact, free fluidity is no longer permitted. They are no longer in suspension, but rest, so to speak, on top of one another. We are entering the range of the formative or plastic

condition. At first the mass is very soft and offers but slight resistance to a change in form, but as the $\frac{\text{water}}{\text{colloid}}$ ratio is still further reduced the mass becomes more stiff and formative. This phenomenon is in harmony with the previously

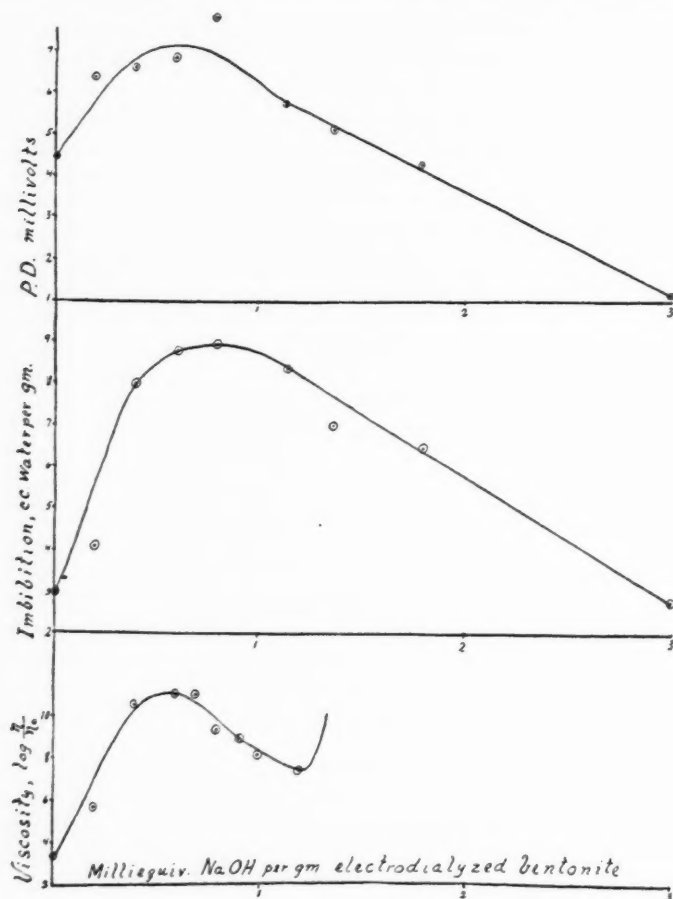


FIG. 3. THE INFLUENCE OF NaOH ON THE P.D., THE SWELLING AND THE VISCOSITY OF ELECTRODIALYZED BENTONITE

expressed views on the micellar structure. In the outer strata of the ion atmosphere the ion density, and hence the osmotic pressure, is very low. The osmotic tension or imbibing force is here correspondingly weak. The osmotically imbibed water is therefore less rigidly held and submits more readily to

shifts and displacements than the deeper layers of water nearer the surface of the particles where the osmotic tension is much greater.

This view on the nature of plasticity is further supported by the fact that clays with a high silica/sesquioxide ratio are more plastic than the clays in which this ratio is low, as was first observed by van Bemmelen (4) and later, in the case of soil colloids, by W. O. Robinson.³ The high-ratio clays contain a higher proportion of exchangeable cations, are more dissociated in water, and disperse and swell therefore more than the low-ratio clays. Further, the plasticity depends upon the nature of the exchangeable cation. The more highly dissociated the exchangeable cation the greater is the plastic range, as in the case of the Na-saturated colloid as compared to the Ca-saturated.

The liquefying effect of adding Na_2CO_3 to a mass of clay (a practice in the ceramic industry) is to be explained as in the case of the viscosity. The salt suppresses the osmotic pressure and hence the swelling of the individual micelles. Other electrolytes do the same, but in most cases the coagulating effect will counteract any liquefying effect. The Na_2CO_3 or silicate fulfill a double function: first, their own coagulating action being weak they precipitate the more powerfully coagulating ions; second, they suppress the volume of imbibed water by suppressing the osmotic pressure.

SWELLING, VISCOSITY, AND POTENTIAL DIFFERENCE

Figures 2 and 3 give a graphic representation of the influence of salts and of NaOH on the swelling, viscosity, and P.D. of the original and the electro-dialyzed bentonite, respectively.

The P.D. values in figure 2 are taken from tables 3, 5, and 6. The actual P.D. between the inside of the gel and the outside solution has not been determined, but the calculated P.D. is equal to $58 \log \frac{x}{y}$, x and y being observed values. The P.D. values in figure 3 are taken from table 13.

The swelling of bentonite in the different salt solutions as shown in figure 2 was determined separately by placing 0.2 gm. of the granulated material in graduated 10-cc. test tubes and carefully adding the different solutions by means of a pipette. The final volume occupied by the gel was recorded as the swelling. In the case of the electro-dialyzed bentonite to which NaOH in varying proportions was added, the swelling—in this case the amount of water imbibed per gram solid—as shown in figure 3 represents the $\frac{\text{water}}{\text{colloid}}$ ratio as given in table 13.

The viscosity curves in figures 2 and 3 were constructed from the viscosities as shown in tables 15 and 16, respectively. The ordinates represent the logarithm of the relative viscosities.

The results are here briefly recapitulated.

³ Unpublished.

The valence effect as shown by the curves in figure 2 is unmistakable. According to theory the P.D. should be more suppressed by the chloride than by the sulfate and should be least suppressed by the ferrocyanide. At the same concentration of the gel, that is, at the same z concentration, the P.D.'s should be in the ratio of 1.0; 1.33; and 1.60, respectively (comp. table 2). This relationship is very nearly approximated in the case of the chloride and the sulfate, the experiment with the ferrocyanide being less accurate as already explained.

Under conditions of free imbibition the valence effect expresses itself in a difference in swelling, the order in which the swelling is suppressed being the same as in the suppression of the P.D.

The descending parts of the viscosity curves show the same order. The increase in the viscosities in higher concentrations is due to the formation of aggregates (flocculation). Here again we meet with a valence effect of the anions. This represents a suppression of the stability of the suspensions. The chloride is the first to flocculate and causes accordingly a more rapid increase in the viscosity. The flocculating power of the sulfate comes next in order, that of the ferrocyanide being the weakest.

This leaves no doubt as to the influence of the valence of the ions having the same sign of charge as that of the colloid. This influence has been denied by Loeb who admits only an influence of the ion in combination with the colloid. Loeb apparently overlooked the fact that the equilibrium equation accounts for the influence of the valence of both ions, the influence being in opposite directions.

The curves in figure 3 show at first an increase in the P.D., the imbibition, and the viscosity as the electrodyalyzed material is being saturated with NaOH. This is accounted for by the formation of a highly dissociated NaOH saturated complex. The maxima coincide with the quantity of base which corresponds to the base exchange capacity. An excess of the base results in a suppression of the P.D., the swelling, and the viscosity, just as when any other electrolyte is added.

SUMMARY

Ions which do not enter into combination with, and are not positively adsorbed by the soil colloids were found to be negatively adsorbed, that is, the concentrations of the ions were found to be greater in the outside solution than in the solution within the gel after equilibrium was established. In the case of the Na-, K-, Ca-, and Ba-saturated colloids, the negative adsorption of the Cl ion in solutions of the respective chlorides was greatest in the Na-colloid-NaCl system and smallest in the Ba-colloid-BaCl₂ system, as shown by the series.



In the case of the NaCl -, NaNO_3 -, Na_2SO_4 -, and $\text{Na}_4\text{Fe}(\text{CN})_6$ -, Na -colloid systems the order of the negative adsorption of the anions is



On the theory that a part of the exchangeable cations exist in a dissociated condition, the underlying principles of this relative order of ion distribution is easily understood. Surrounding the soil particle, i.e., in the micellar solution, there is an excess of cations. This must lead to an unequal distribution of the free electrolyte between the micellar and intermicellar solutions according to the laws of the Donnan equilibrium. The application of the equilibrium formulas on the valence effect showed a fair agreement between theoretical and observed differences.

Special attention was given to the valence effect of the anions, i.e., the ions of the same sign of charge as the colloid because of the denial of Loeb of any such effect. But it has been shown that the equilibrium equation demands, and that the experimental data prove a valence effect of these ions. This effect is opposite to that of the cations, i.e., the ions of opposite sign of charge to the colloid.

In the absence of free electrolyte the P.D., the swelling, and the viscosity are alone governed by the degree of dissociation of the exchangeable cations. The greater the dissociation the greater is the imbibition of water, which proceeds until there is an equilibrium between the osmotic and electrostatic forces. The dissociation depends upon the specific nature of the cations such as hydration and potential, and not merely on the valence. It is in this relationship that the ions arrange themselves in the order of the Hofmeister or lyotropic series.

In the presence of free electrolyte, the P.D., the swelling, and the viscosity are suppressed and this suppression depends solely on the valence of the ions in accordance with the thermodynamic and osmotic equilibrium equations. The Donnan equilibrium is to be dealt with as an effect and not as a cause. It does not create the aforementioned phenomena but is merely related to their suppression. All are effects of the same cause, namely, the formation of an ion atmosphere around a colloidal particle, i.e., the colloidal micelle.

When the gel is free to swell the valence effect shows itself in differences in the swelling or imbibition. If the swelling is inhibited, i.e., when the gel concentration is kept constant, the valence effect shows itself in differences in the negative adsorption, i.e., in the values of $\frac{x}{y}$ and in the P.D.

The colloidal micelle may be likened to a living organism. It reacts to any change in the surrounding medium only more quickly because it possesses no membrane. Remove the water and the micelle is destroyed leaving an inert particle comparable to the spore of an organism. This process is reversible. In dilute solutions (hypotonic) it swells, in strong solutions (hypertonic) it shrinks, thus striving to maintain a definite osmotic pressure and P.D. with respect to the outside solutions.

Distinction must be made between two forms of soil solution. The micellar solution is an integral part of the micelle. Any attempt to remove this solution by pressure or by any other means must fail.

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A STUDY OF DIASTASE ACTIVITY IN PLANTS: THE EFFECT OF PHOSPHATES IN THE SOIL MEDIA

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Received for publication March 25, 1929

In an earlier paper (2) the results of a study of the effect of increasing amounts of potassium salts in the soil media upon the diastase activity of nasturtium plants were reported. No definite evidence of an expected correlation between the amount of potassium salt applied and activity was found but there appeared to be a correlation with favorable growing conditions, as was indicated by height, appearance, and dry weight data. Since a number of samples of soybeans which had been grown with a varying phosphate treatment were available¹ for study, it appeared of interest to determine the relative activity of these to see whether the correlation between favorable conditions for growth and diastase activity would be similarly evident under phosphate treatments.

PRODUCTION AND PREPARATION OF THE SOYBEAN MATERIAL

The plants were grown in the greenhouse in pot cultures. Mono-calcium and rock phosphates were applied at the rate indicated in table 1. The roots and tops were separated when cut and were dried in paper sacks hung in the greenhouse for about a month. The samples were ground and the phosphorus content and diastase activity determined.

DETERMINATION OF DIASTASE ACTIVITY

In the beginning an effort was made to use an extract of the soybean material, following the general procedure of Oshima (3), for the determination of diastase activity. However, when 2.5 gm. of the sample was extracted with 100 cc. of water for 3 hours a 70-cc. portion of the filtrate had a negligible action on starch solution. Accordingly, much the same method followed in the earlier paper was used:

PROCEDURE

A 0.5-gm. sample of the plant material was weighed into a small Erlenmyer flask. From a pipette, 100 cc. of 2 per cent starch solution was introduced,

¹ The samples were grown, harvested, and analyzed for phosphorus by Mr. H. A. Lunt in connection with certain problems which he had under investigation. We are greatly indebted to him for his kindness in giving them to us for this study.

4 or 5 drops of toluene added, and the mixture shaken. At the same time a blank was prepared in the same way and immediately 10 cc. of 2N NaOH added. Digestion of the sample was allowed to proceed for 3 hours at 40°C., then the enzymatic action was stopped by adding 10 cc. of 2N NaOH. Apparent dextrose was determined on an aliquot portion by Defren's (1) method as in the earlier work. To insure the absence of particles of plant material a short piece of rubber tubing holding a small plug of absorbent cotton was

TABLE 1
Diastatic activity of soybean plant material grown in soil treated with varying amounts of phosphates

SAMPLE	PHOSPHATE TREATMENT	TOPS			ACTIVITY	RATIO
		Green weight	Dry weight	Dried material		
Acid phosphate						
	lbs. per acre	gm.	gm.	per cent P.		
2	No P	20.5	5.8	0.076	1.241	100
3	5	38.5	10.6	0.090	1.487	120
4	5	42.0	12.0	0.088	1.426	115
7	15	91.0	27.7	0.096	1.244	100
8	15	98.5	28.5	0.096	1.307	105
9	15	90.0	27.0	0.106	1.303	106
5	25	111.0	33.0	1.128	1.359	110
6	25	123.5	36.5	0.120	1.430	115
10	150	158.0	44.5	0.293	1.187	96
11	150	147.0	40.0	0.316	1.025	83
12	150	166.0	45.7	0.332	0.961	77
Rock phosphate						
13	500 R.P.	20.5	5.7	0.062	1.451	101.0
14	24.0	7.0	0.055	1.429	99.5
15	21.0	6.4	0.052	1.439	100.0
16	2000 R.P.	25.0	8.3	0.056	1.416	98.5
17	28.0	8.2	0.069	1.461	101.5
18	24.0	7.0	0.070	1.572	102.0

placed over the tip of the pipette while the aliquot was being withdrawn. Although the reducing value of the mixture of the hydrolytic products of starch is usually expressed as maltose, for comparative work of this type it makes no difference in terms of which sugar it is expressed. If desired, the "apparent" maltose can be calculated by use of its reducing ratio to glucose.

The grams of apparent dextrose which would have been produced by 1 gm. of the soybean material under the conditions of the experiment represents the "activity" of the sample.

The results of the determinations are given in table 1. To sample number 2 the no phosphorus treatment, is arbitrarily assigned an activity of 100 and the

acid phosphate samples are compared to it. In the rock phosphate series sample number 15, which has the lowest phosphorus content, is the standard of reference.

DISCUSSION OF RESULTS

In the table it is apparent that the amount of phosphorus taken up by the plant is roughly proportional to the amount of acid phosphate applied. The growth of the plants as indicated by dry weight production is also of this general agreement. Although the plants receiving the equivalent of 5-25 pounds of acid phosphate per acre tend to show a slight increase in diastase activity over the no phosphorus plants, the variations are not consistent and have no close relation with increase in dry weight. With the equivalent of 150 pounds of acid phosphate per acre, the activity falls off with an increase in the phosphorus taken in, even though the dry weight production still increases. This seems to indicate that diastase activity is not related to favorable conditions for growth alone but also to other factors. The decrease in activity and growth noted in the previous paper was undoubtedly due to over-feeding phenomena. A close relationship between diastase activity and potash nutrient is still probable. It appears that the high concentration of acid phosphate in the soil solution has a slight detrimental effect upon the elaboration of diastase, although small or moderate amounts may have a slight beneficial effect.

With the rock phosphate treatments the differences to be noted as regards phosphorus taken in, dry weight produced, and diastase activity are no greater than the experimental error.

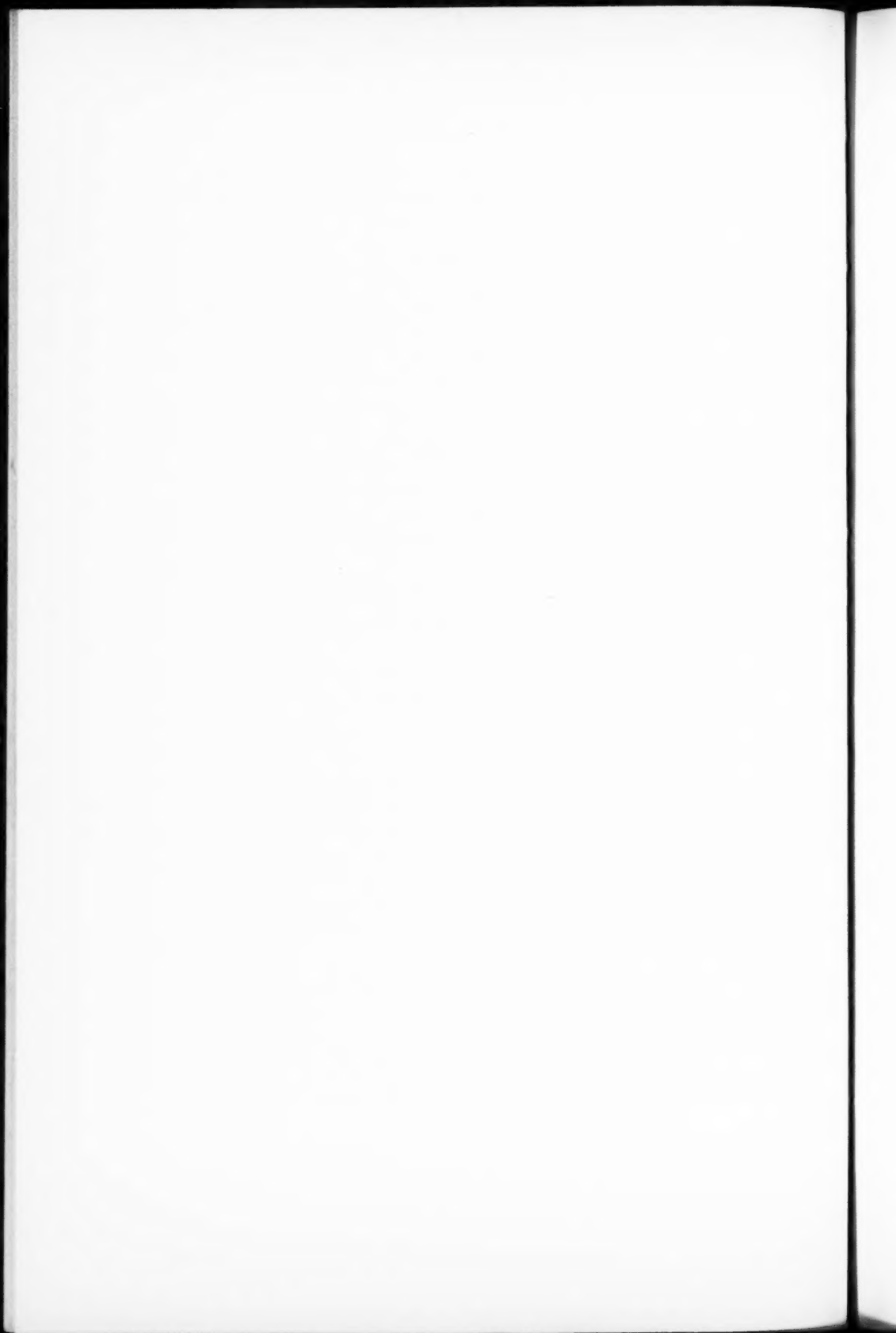
SUMMARY

Soybeans were grown in the greenhouse in pot cultures with different amounts of acid phosphate fertilizers. Although the dry weight and phosphorus taken into the plant increased markedly with increasing applications of the fertilizer, the changes in diastase activity were slight for moderate amounts. With large amounts the activity seemed to fall off even though the dry weight and phosphorus taken in still increased.

With rock phosphate no significant differences in any respects were observed between the untreated and treated pots.

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A METHOD FOR THE DETERMINATION OF TOTAL CARBON AND ALSO FOR THE ESTIMATION OF CARBON DIOXIDE EVOLVED FROM SOILS

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Received for publication April 1, 1929

The titrimetric method has greatly simplified the estimation of carbon dioxide. Truog (12) has shown that the bead tower facilitates and hastens the absorption of carbon dioxide and that the single titration (8, 9, 13) is to be preferred to the double titration method (2, 3, 6, 7). A very simple trap for the absorption of carbon dioxide has been devised which combines the single titration with the use of the bead tower and sodium hydroxide. This trap and the method described may be used for the estimation of carbon dioxide from various sources, such as the carbon dioxide evolved from the soil by biological processes or from the combustion of organic materials by the wet method² (1). The details of the apparatus and its operation are given in this paper.

APPARATUS ADAPTED TO THE CHROMIC ACID METHOD FOR TOTAL CARBON³

The details of this apparatus are shown in figure 1. A 200-cc. Erlenmeyer flask (*D*) is closed with a 3-hole rubber stopper into which is fitted an inlet tube (*B*) leading from a soda-lime tube (*A*), a 12-inch water cooled condenser (*E*) with a rather small bore inner tube and a separatory funnel (*C*) through which the reagents are introduced. The inlet tube is so adjusted that it extends to a point near the bottom of the flask (*D*). The lower end of the condenser (*E*) is drawn out and a hole blown in the side so as to facilitate the free passage of gases with no interference from the condensed liquid.

The fume trap. At the top of the condenser (*E*) is fitted a U-tube (*F*) so arranged as to form a double trap to remove the chlorine and sulfuric acid fumes from the gas. This trap follows somewhat the plan of White and Holben

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² There are indications that substances like alcohol or acetic acid are not completely oxidized by the wet method but are partially volatilized from the oxidizing solution.

³ While this paper was in press, an article appeared by T. E. Friedemann and A. I. Kendall [The determination of carbon and carbon dioxide. *Jour. Biol. Chem.* 82: 45-55 (1929)] in which a similar apparatus is described for the determination of total carbon and carbon dioxide. These authors also report the recovery of 99 to 100 per cent of the carbon as carbon dioxide from acetic acid and ethyl alcohol by the use of a high concentration of sulfuric acid in the oxidizing mixture.

(14). The bottom of the U-tube is filled with glass beads and above these in each arm is placed a small loose plug of glass wool. The first arm (*F1*) is filled with 20-mesh pumice saturated with a concentrated solution of silver sulfate, and the second arm (*F2*) with pumice saturated with concentrated sulfuric acid which has been boiled for two hours to remove the dissolved

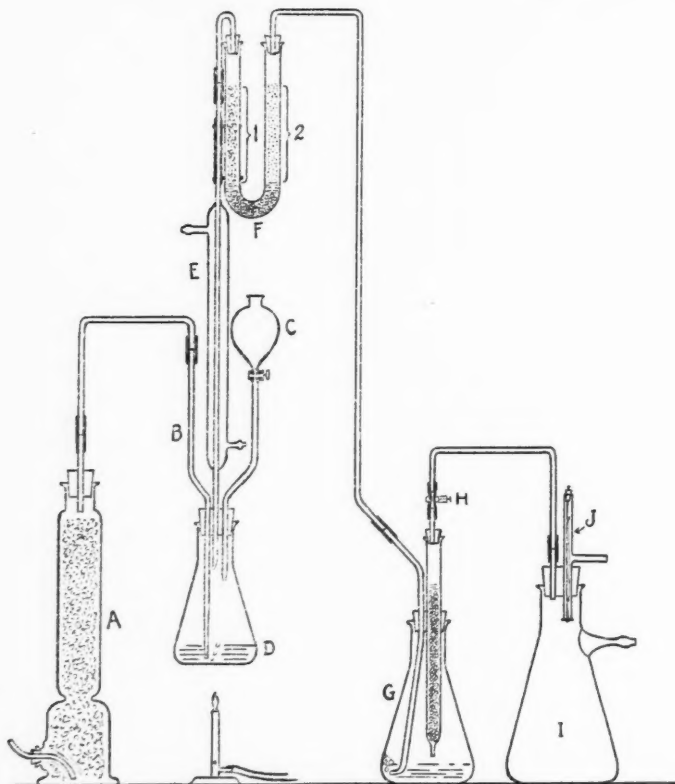


FIG. 1. APPARATUS, INCLUDING A NEW CARBON DIOXIDE TRAP, FOR THE DETERMINATION OF TOTAL CARBON BY WET COMBUSTION

gases. The silver sulfate removes the chlorine, and the sulfuric acid the sulfurous acid fumes. The contents of this trap are easily replaced and should not be used too long. This "dry" trap allows free passage of gases and removes all danger from back pressure which may be encountered with the wet trap.

The carbon dioxide trap. This trap (*G*) is adapted to the single titrimetric estimation of carbon dioxide and to the use of sodium hydroxide. It works on the same principle as the Truog (12) trap but is simpler and operates more

rapidly. The materials necessary for its construction are few and simple: a 300-cc. Erlenmeyer flask, a $\frac{3}{4}$ x 10 inch test tube, a number 6 rubber stopper, a little glass tubing, and a few glass beads. By means of a blast lamp, the test tube is drawn out at the bottom, and while still hot the upper part of the constriction is flattened so that two beads will lie at the bottom and allow a free passage of fluid either way. This point is important as it is necessary that all of the solution in the tower be easily washed down into the flask. The opening in the bottom of the tower should be large enough to allow rapid washing. Four- to six-millimeter solid glass beads are most satisfactory. The lower end of the entrance tube of the trap is drawn out and bent toward the side of the flask so that as the bubbles emerge from the tip they adhere for a time on the side of the flask before diffusion. The exit from the trap is made through the bead tower where the last traces of carbon dioxide are absorbed. This trap will handle gas flowing at the rate of 4 to 8 or even more bubbles per second, but usually a less rapid flow is more satisfactory. The rate of the gas flow is regulated by the screw-cock (*H*) and the extent of the vacuum by the valve (*J*). This valve is made by holding a thin rubber disk against the lower end of a glass T-tube by the aid of a light rubber band, two pins, and a small cork. By moving the upper pin up or down through the cork, the valve can be regulated for any desired pressure and the water in the suction pump may be allowed to run more rapidly than if the valve is not used. This valve will maintain a constant pressure and remove any danger of back suction even if the water pressure does vary somewhat.

Method of operation. The charge is placed in flask (*D*) which is then attached to the apparatus. The amount of material used is governed by the amount of carbon which it contains. From 20 to 100 mgm. of carbon are convenient amounts with which to work, but more may be used if necessary; the method is also accurate with smaller amounts. To the carbon dioxide trap (*G*) is added a measured quantity of 0.5 *N* carbon-dioxide-free sodium hydroxide. The amount added should be in excess of the amount necessary to absorb all of the carbon dioxide as sodium carbonate. The volume is made up to about 40 to 50 cc. with carbon-dioxide-free distilled water. On starting the flow of gas, the bead tower is allowed to dip into the solution until the liquid reaches the top of the beads. The tower is then raised and no more solution is allowed to enter. A little glycerol between the glass tower and the rubber stopper facilitates the adjustment of the tower. The flow is then regulated to about 3 to 5 bubbles per second. The oxidizing solutions are then introduced into the flask (*D*) through the separatory funnel (*C*). The oxidizing mixture is heated as rapidly as possible but not so as to cause it to back up into the inlet tube. A flow of air into flask (*D*) should always be maintained. The content of flask (*D*) is brought to boiling and boiled for 10 or 15 minutes or until all of the carbon dioxide has been driven off.

The carbon dioxide trap (*G*) is then detached and all of the alkali from the bead tower and entrance tube is washed into the flask with carbon-dioxide-free

distilled water, a supply of which may be obtained conveniently from an elevated carboy. An excess of neutral 2 *N* barium chloride is added and the excess alkali titrated with 0.5 *N* carbon-dioxide-free hydrochloric acid with phenolphthalein as the indicator. The difference between the amounts of alkali and acid used, multiplied by three, gives the milligrams of carbon. One cubic centimeter of 0.5 *N* sodium hydroxide is equivalent to 3 mgm. of carbon or 11 mgm. of carbon dioxide. For this method there should always be a blank determination so as to deduct the carbon dioxide in the apparatus and the reagents.

APPARATUS FOR THE ESTIMATION OF CARBON DIOXIDE EVOLVED FROM SOILS

The evolution of carbon dioxide from a soil is one of the best indices of its biological activities. For the study of the respiration of soil microorganisms it is necessary to have a rapid and accurate method for estimating the carbon dioxide evolved. For this purpose, the carbon trap and method just described have been used to advantage in previous work (4). The equipment is inexpensive and simple in its construction, being made up of ordinary laboratory supplies, and the system allows itself to be added to until large numbers can be run at one time. Sets of 40 to 60 or more units can be aspirated at the same time from one small pump, and as many as 50 or more carbon dioxide determinations made in a 4-hour period.

Aspiration. Various methods of aspiration have been used for collecting carbon dioxide from soil. The aspiration may be either continuous or intermittent. When continuous, a steady flow of air at a rate of about one or two liters an hour is maintained through the aspiration chamber. With the intermittent system, aspiration is maintained for a few minutes once or twice a day and the chamber is closed for the remainder of the time. The intermittent system has the disadvantage of a heavy accumulation of carbon dioxide between aspirations. At times, in fact, this accumulation is so great that anaerobic conditions are approached and the activities of the microorganisms greatly inhibited. Under these conditions the carbon dioxide liberated for any given period may be lowered by one-half.

The aspiration may be directly over the soil (2) which is placed in a flask, or the air may be drawn through an aspiration chamber such as a bell jar or similar equipment in which a pot or beaker containing the soil is placed (8, 9, 10, 13). Other workers (3, 6, 7) have drawn the air directly through the soil which is placed in a cylinder or similar container. Aspiration over the soil permits the diffusion of carbon dioxide which would occur under normal field conditions, but when the air is drawn through the soil there is an abnormal soil atmosphere with either intermittent or continuous aspiration. Continuous aspiration through the soil gives too much oxygen and the intermittent system gives long intervals of diminished diffusion and high carbon dioxide concentration interspersed with one or two short daily intervals of high oxygen content.

It seems, therefore, that the most nearly normal and uniform soil atmosphere is maintained by a slow continuous aspiration of carbon-dioxide-free air over the soil. The carbon trap described is well adapted to this sort of aspiration. A very satisfactory continuous aspiration for large numbers of flasks is maintained by means of a small suction pump having a constant pressure valve (*G*, fig. 2) on the suction flask (*F*).

Operation. The details of the set-up for carbon dioxide evolution from soils are shown in figure 2. The air enters the scrubbing train through the soda-lime tube (*A*). If large numbers of determinations are being made at the same time, one or more soda-lime tubes may be added to care for the extra volume of air. Soda-lime is preferable to potassium hydroxide solution because it gives a freer passage of air with less danger of stoppage or back pressure. The air then goes to tower (*B*), which is filled with coarsely granulated pumice saturated with

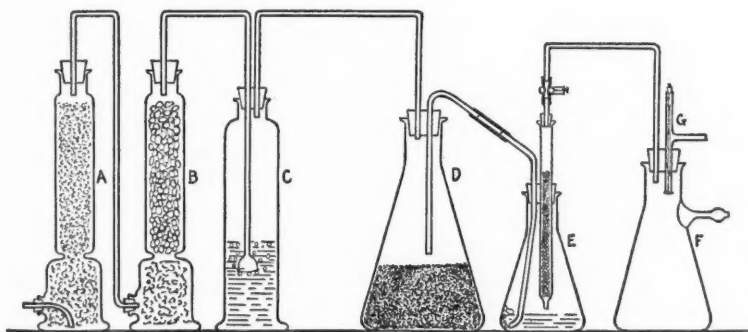


FIG. 2. APPARATUS FOR THE ESTIMATION OF CARBON DIOXIDE EVOLVED FROM A SOIL

sulfuric acid (dilute 1-2). This tower removes the ammonia. Tower (*C*) is partly filled with a dilute solution of barium hydroxide and the air is bubbled through this solution. The prime purpose of this tower is to saturate the atmosphere with moisture so that as much moisture is carried into the soil flask as is carried out of it. By this means a 600-gm. sample of soil has been carried for a month without loss of moisture. The barium hydroxide is introduced into tower (*C*) to serve as an indicator in case the contents of tower (*A*) become spent and allow the carbon dioxide to pass. At the same time it acts as an emergency carbon dioxide trap in the scrubbing train. Two units of (*C*) may be used if desired.

The carbon-dioxide-free air, now saturated with moisture, enters the soil flask (*D*) at the top and the carbon-dioxide-laden air is drawn off just above the soil surface. It is well not to have the outlet tube nearer to the soil than about one-half inch, as drops of moisture will sometimes collect at the bottom

of the tube and if these drops touch the soil, stoppage may occur. The soil containers used in this case were 750-cc. Erlenmeyer flasks with 600 gm. of soil, but this is a matter of adjustment to suit conditions. The carbon-dioxide-laden air passes into the carbon dioxide trap (*E*) where the carbon dioxide is absorbed. At the end of the aspiration period the traps are removed in pairs and the carbon dioxide determined as already outlined.

DISCUSSION

The use of sodium hydroxide in place of barium hydroxide has three distinct advantages: (a) The solution may be more concentrated; (b) the carbonate

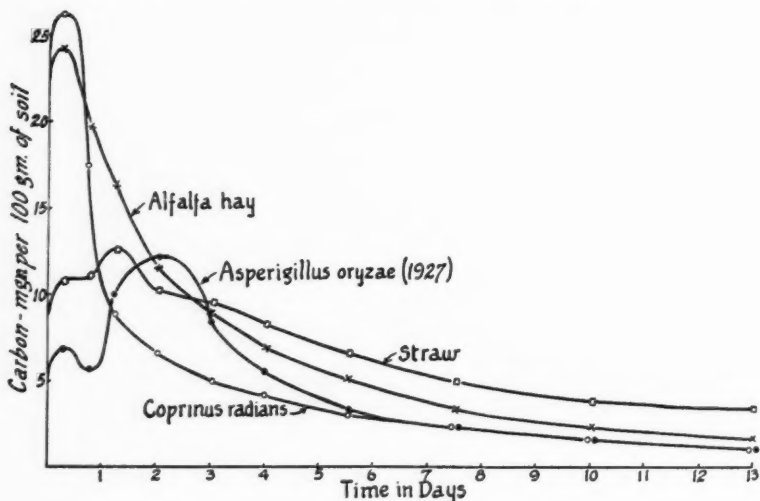


FIG. 3. RATE OF EVOLUTION OF CARBON DIOXIDE FROM VARIOUS SUBSTANCES

The amounts of organic materials varied but each substance contained 10 mgm. of nitrogen

does not precipitate and the solution in the bead tower can be washed out easily with water without removing the beads; and (c) if insufficient sodium hydroxide is used in the trap to absorb all of the carbon dioxide as the carbonate, some will be absorbed as the bicarbonate, thus increasing the capacity of the absorbing solution. Ledig (5) has shown that potassium hydroxide absorbs carbon dioxide more rapidly than does sodium hydroxide, but it was found in this work that sodium hydroxide gave perfect absorption. Carbon-dioxide-free sodium hydroxide is also more easily prepared than the carbon-dioxide-free potassium hydroxide because sodium carbonate is less soluble than potassium carbonate.

In the presence of large amounts of barium carbonate the color change of phenolphthalein is not so sharp as one would like, and the titration should not

be hurried especially on nearing the end point. With white artificial light or good day light, the titration should be carried on until the pink color has entirely disappeared. Schollenberger (11) recommends thymolphthalein in place of phenolphthalein because of the higher pH value of its end point. The author, however, prefers phenolphthalein, with which an accuracy of from 0.1 to 0.4 mgm. of carbon may easily be obtained.

Plate 1 shows 42 flasks and carbon traps operating on one pump and attached to one scrubbing train. The rate of evolution of carbon dioxide from organic materials placed in the soil is shown in figure 3. During the early periods when the carbon dioxide evolution is high, the intervals between analyses may be as short as 8 or 12 hours, and as the evolution decreases the intervals may be lengthened to several days or a week if desired.

SUMMARY

A rapid method for the estimation of carbon dioxide is given. This method is applicable to the determination of organic carbon, carbonate carbon, or the carbon evolved from a soil as carbon dioxide. A total carbon determination can be made in about 45 minutes and carbon dioxide determinations at the rate of about 10 to 20 an hour.

A simple carbon dioxide trap is described which combines the bead tower and the use of sodium hydroxide with the single titration principle. The carbon dioxide is absorbed in 0.5 *N* sodium hydroxide solution and precipitated as the carbonate by the addition of an excess of 2 *N* neutral barium chloride. The excess alkali is then titrated with 0.5 *N* hydrochloric acid, phenolphthalein being used as the indicator. The difference between the cubic centimeters of standard alkali and acid used, multiplied by 3, gives the milligrams of carbon.

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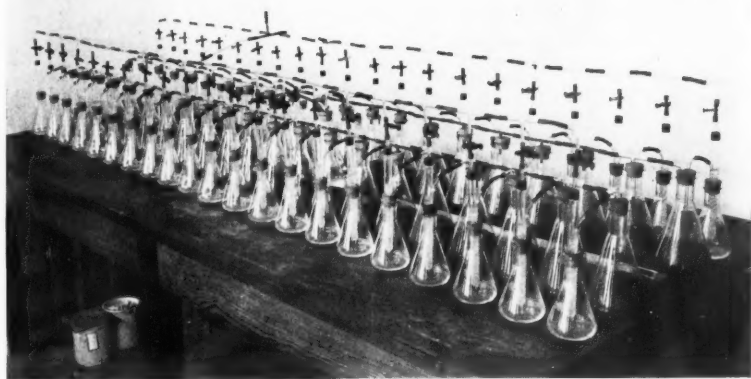
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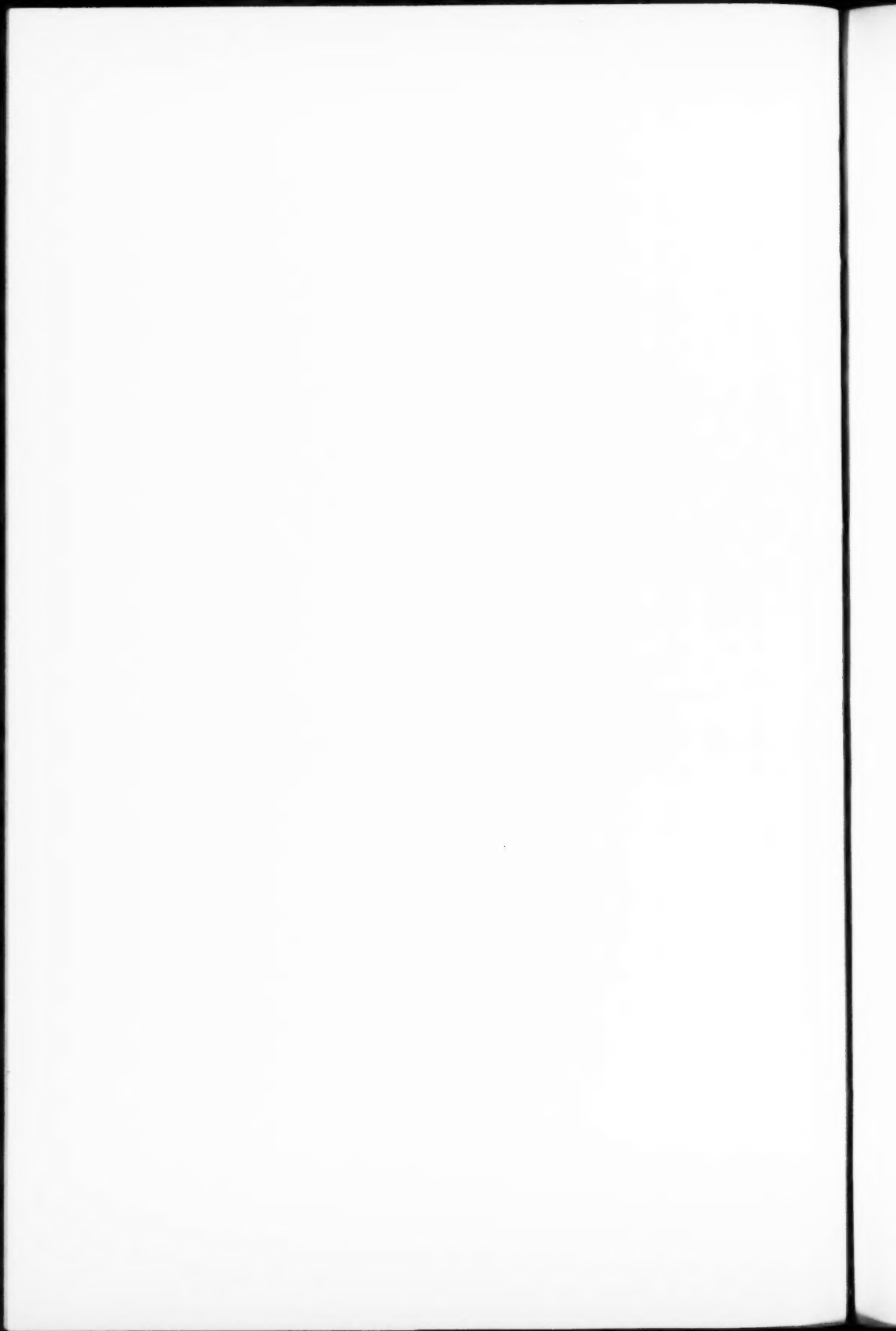
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PLATE 1

SET-UP USED IN CARBON DIOXIDE EVOLUTION FROM SOILS

A. FLOYD HECK





COLLOIDAL PROPERTIES OF WILLAMETTE VALLEY SOILS

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Received for publication April 4, 1929

A very much more definite knowledge of the meaning of acid and alkali soils has resulted from increased knowledge of the colloidal fraction of the soil. The retention of essential nutrient anions by the soil is much better understood since recent developments in the field of soil colloids. Though there is a tendency to overemphasize certain phases of work at certain times, it seems reasonable to assume from our present knowledge, that most of the chemical and physical properties of soils are in some way connected rather intimately with the amount and condition of the colloidal fraction. Knowledge of the colloidal properties of soils is therefore of great practical and scientific interest. This study was planned especially to observe correlations between chemical and physical properties of soils and their colloidal components.

PLAN OF STUDY

The following nine soils were selected for study: Chehalis Fine Sandy Loam, Cove Clay, Willamette Silty Clay Loam, Dayton Silty Clay Loam, Aiken Clay Loam, Olympic Clay, Melbourne Silty Clay Loam, Peat, and Muck. All soils except the peat and muck were sampled by horizons, so that each horizon of the profile could be studied separately.

Two of these soil series, Chehalis and Cove, are recent formations. The Chehalis is a free working, well-drained and highly productive soil. The Cove on the other hand is very heavy and tight, difficult to till, but fertile when once in crop.

Two series, the Willamette and Dayton, are old valley-filling or high terrace formations. The Willamette is a well-drained, highly productive, and desirable agricultural soil. The Dayton on the other hand is poorly drained, and underlaid with a sticky blue clay that makes it difficult to till and rather undesirable as an agricultural soil.

Two series, Aiken and Olympic, are residual hill soils from igneous rocks, largely the product of the weathering of basalt. Both are rather desirable agricultural soils, with good drainage, and are fairly fertile when well farmed. The chief outward distinction is the red color of the Aiken in contrast to the brown color of the Olympic.

The Melbourne series is likewise a residual hill soil, but is formed from

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sedimentary instead of igneous rock. The underlying sandstones are sometimes rather close to the surface, but on the whole the Melbourne is a desirable soil.

Two organic soils, a Lake Labish Peat and a Clackamas County Muck, were included in part of the studies to observe characteristics which might be related to their organic nature. The soils were sampled and stored outdoors in large jars to maintain a moist condition throughout the period of study.

The study included a determination of the amount of colloid in the different horizons of all soils, together with a study of the chemical composition of both the colloid and the whole soil. For this phase of the work, iron, aluminum, silica, and calcium were determined so that any relations which might exist between composition and physical properties might be observed. There was included also a study of exchangeable calcium, and the retention of one anion, PO_4 , by the colloids and the whole soils.

Because of the laboriousness of the task and the limitations of time, the colloidal material separated from the three horizons of only one soil series, the Chehalis. The data are therefore inadequate for definite conclusions at the present time.

EXPERIMENTAL

Isolation of colloids

The definition for "soil colloid" is somewhat arbitrary. The Bureau of Soils (7, 8) defines the colloidal material on the basis of the size of particles and selects one micron as the upper limit for colloidal size. Their method for separating the colloid from coarser material was employed except that fresh moist soils were used and the period of sedimentation was 10 days, as recommended by Bradfield (3). After passing through the supercentrifuge once the colloidal suspension was deep amber in color, and contained a little more than 0.3 per cent solid matter. After a second centrifuging the suspensions were lighter in color and contained about 0.05 per cent of solid matter. When filtered on the Pasteur-Chamberlain filter, a clear filtrate resulted, and the colloidal mass remaining on the candles was a reddish amber, jelly-like mass. When dry the jels formed hard, horny, brittle masses.

Properties of colloids

Largely because of lack of suitable methods for accurate determinations, early workers often placed the quantity of colloidal material in soils at no more than 0.5 to 2 per cent.

The chief difficulty lay in the practical impossibility of dispersion of colloidal material and therefore the inability to separate any appreciable amount by sedimentation methods. Since indirect methods have been devised, based upon specific properties of colloids, more reliable information has been obtained and much larger amounts of colloid are found to be present in the average good

soil. After trying various methods the water vapor absorption method was found fully as satisfactory as any by Gile et al. (8).

The water vapor method was used in the following study, practically as planned by them (8, 9). Since the colloidal material was separated from the three horizons of only one soil, the Chehalis, only for these three colloids could

TABLE 1
*Amount of colloid found by the water vapor method**

SOIL TYPE	HORIZON	PER CENT COLLOID
Chehalis Fine Sandy Loam.....	I	22.8
	II	25.7
	III	25.1
Cove Clay.....	I	42.7
	II	65.8
	III	62.4
Willamette Silty Clay Loam.....	I	20.7
	II	20.2
	III	29.7
Dayton Silty Clay Loam.....	I	25.3
	II	42.2
	III	51.1
Aiken Clay Loam.....	I	39.5
	II	42.5
	III	51.8
Olympic Clay.....	I	50.8
	II	55.9
	III	58.0
Melbourne Silty Clay Loam.....	I	30.2
	II	42.8
Peat.....		95.6
Muck.....		71.4

* Most of the analytical data in this paper was supplied by T. M. Tieh, a graduate student in the department of soils.

the specific absorption be determined. It was found to be for the surface horizon 0.263, subsoil 0.283, and parent material 0.284. Robinson (9) working with 34 colloids from different soils reports a range from 0.240 to 0.348. The mean specific absorption was 0.298.

In this work the mean specific absorption of 0.298 obtained by Robinson (9) was used as a basis for calculation in all determinations except for the Chehalis soil, for which the specific absorption was determined.

Table 1 shows the amount of colloid found in the various horizons of the different soils by this method.

It will be observed that the amount of colloid is rather large but correlates fairly closely with field texture. Robinson's data (9) show that percentage of colloid is rather uniformly higher in the subsoil, which under natural conditions in mature soils is heavier in texture than the surface. Out of 15 soils studied by Robinson (9), 13 show more colloid in the subsoil.

In every case except the Willamette in this study, there is appreciably more colloid in the subsoil. There may be a question whether the profiles as found are the result of maturity, or simply the result of deposition. Why the deep formation or parent material should show more colloid than is found in the

TABLE 2
Composition of soil colloid

SOIL TYPE AND HORIZON	ORGANIC MATTER	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	
Chehalis.....	I	3.72	40.01	24.80	11.37	1.48
	II	3.60	38.37	23.39	10.48	1.48
	III	2.40	41.21	25.01	12.00	1.51
Average of 45 soils—Bureau of Soils (10).....	4.02	43.34	26.83	10.70	1.05	

TABLE 3
Relation of composition of colloids

CHEHALIS HORIZON	$\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3}$	$\frac{\text{CaO}}{\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3} \times 10$
I	2.11	0.84
II	2.16	0.89
III	2.11	0.84

subsoil can not be fully explained. Both organic soils necessarily show a high colloid content, since organic matter in the humified condition and even in the raw state, is colloidal in nature.

Chemical composition of soils and colloids

The data in table 2 in comparison with that in table 4 show that the colloidal material is higher in organic matter, lower in silica, somewhat higher in aluminum, and considerably higher in iron, but much lower in calcium than the whole soil. The percentage of total calcium in the whole soil is unusually high, however. When the data are compared with the average of 45 determinations by the Bureau of Soils (10) as shown in table 2, the results for the colloidal material are found to correspond closely.

Various workers have noted a correlation between the properties of soils and the chemical composition of the colloidal material (1, 6) especially when the ratio

$$\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3} \text{ was studied and compared with the ratio } \frac{\text{CaO}}{\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3}.$$

TABLE 4
Comparison of the soils

SOILS		ORGANIC MATTER	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO
		per cent	per cent	per cent	per cent	per cent
Chehalis	I.....	1.99	55.64	21.08	8.37	5.77
	II.....	2.09	55.12	22.87	8.28	6.00
	III.....	1.25	55.63	20.49	9.09	5.38
Cove	I.....	4.87	51.85	19.37	12.92	3.19
	II.....	0.94	52.81	21.99	13.54	2.86
	III.....	0.60	53.52	19.23	14.13	4.13
Willamette	I.....	3.91	63.41	12.15	10.89	1.88
	II.....	1.54	66.23	16.43	8.43	1.75
	III.....	0.79	63.18	13.11	13.64	3.39
Dayton	I.....	3.70	66.84	17.55	5.49	2.62
	II.....	1.03	66.12	16.71	6.91	1.97
	III.....	0.38	59.48	17.97	7.92	2.82
Aiken	I.....	3.07	47.15	22.80	16.74	0.66
	II.....	1.78	47.28	21.83	17.52	0.39
	III.....	1.03	55.99	24.14	18.44	0.48
Olympic	I.....	3.50	46.54	18.77	18.32	4.23
	II.....	1.70	49.97	19.09	17.79	3.44
	III.....	1.18	46.91	12.47	22.28	3.20
Melbourne	I.....	3.26	64.30	17.91	8.55	0.61
	II.....	1.39	61.92	18.81	8.46	0.80
Peat.....		72.63				
Muck.....		46.10				

The data in table 3 are too limited for study except by comparison with other available data. By comparing with results obtained by the Bureau of Soils (6) it is found that the ratio noted in table 3 places this soil in an intermediate group. The highest ratio reported by Gile (6) for aluminum and iron to silica was 3.62 while the lowest was 0.54. The ratio noted in table 3 is 2.11 with very little difference in the various horizons. The same may be said for the molecular ratio of aluminum and iron to calcium. The highest ratio reported

by Gile is 1.81 and the lowest 0.18. The ratio found here is 0.84 with little variation in the different horizons.

In a study of humid-tropical and humid-temperate soils Bennett (2) found close correlation between the physical properties of the whole soils and their chemical composition. On the basis of physical behavior as correlated to chemical composition he made two groups; namely, friable soils in which the ratio of $\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3} =$ less than 2, and plastic soils in which the ratio was greater than 2.

The average of 24 friable tropical soils showed 29.30 per cent SiO_2 ; 14.91 per cent Fe_2O_3 ; and 34.28 per cent Al_2O_3 , with 0.24 per cent of calcium. Other soil bases averaged correspondingly low. These are lateritic soils.

TABLE 5
Relation of composition of soils

HORIZONS	$\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3}$	$\frac{\text{CaO}}{\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3} \times 10$
Chehalis I.	3.57	3.98
Cove I.	2.97	2.10
Willamette I.	5.62	1.79
Dayton I.	5.38	2.27
Aiken I.	2.38	0.36
Olympic I.	2.59	2.50
Melbourne I.	4.66	0.48
Average.	3.88	1.92

The average for 24 non-friable tropical soils was 52.33 per cent SiO_2 ; 9.53 per cent Fe_2O_3 ; and 21.28 per cent Al_2O_3 ; and 1.55 per cent CaO , with other bases correspondingly higher than in the friable group.

The data in table 4 in comparison with these figures show that the soils under study resemble the non-friable group in composition to a much greater extent than the friable group.

The friable group is described as lateritic, very porous, deep, and uniform, high in colloidal content yet flocculated and granular. Though the data presented here are far too meager for definite conclusions, the two hill soils, Aiken and Olympic, show only slight lateritic tendencies in their slightly lower SiO_2 content and higher Fe_2O_3 content. These soils are somewhat friable, and inclined to good to excessive drainage.

The SiO_2 of all other samples was about as high as, and in most cases much higher than even that of the non-friable group, studied by Bennett. The Al_2O_3 and Fe_2O_3 contents, likewise, place most of the other soils decidedly in the non-friable group. Exceptions are the somewhat lower iron content of the Willamette and the somewhat lower silica content of the Cove series. These ex-

ceptions, however, do not appear significant. The general physical properties of these soils place them decidedly in the non-friable group.

The molecular ratios in table 5 show that in no case is the ratio $\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3}$ less than 2, but is closest to it in the Aiken and Olympic series. The ratio found by Bennett (2) for the average of the friable group was 1.25 while for the plastic group it was 3.71. In only one of these soils, the Aiken, does the ratio $\frac{\text{CaO}}{\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3}$ appear to be especially low. It is rather low also in the Melbourne series, but with only meager data such variations are not necessarily typical.

Study of the different horizons of the various soils does not bring out any striking characteristics. The recent soils, as might be predicted, are rather more uniform in the composition of the different horizons than the older, more mature soils. With the exception of the Chehalis series, most of the organic matter is found in the surface horizons. In spite of leaching there remains as much lime in the surface as in any horizon in most cases.

There is noticeable absence of correlation between color and composition. Aiken, because of its bright red color, is locally known as a red-hill soil. Olympic on the other hand, which is a rich brown, contains slightly more iron. Cove, which appears rather uniformly black in color as deeply as it was sampled, contains five times as much organic matter in the surface horizon.

Base exchange

Exchangeable calcium was studied on the colloidal material from the different soil horizons and on the different horizons of all the soil series. These data are compared with the total calcium and with the reaction of the soil (table 6).

It is quite noticeable that a very large percentage of the calcium of the colloidal material is exchangeable whereas a rather small percentage of the calcium of the soil as a whole is exchangeable. This corroborates the oft made claim that the exchangeable and easily available calcium is practically all held by the colloidal complex, and that good soils must be abundantly supplied with this nutrient so held.

Aiken and Melbourne which have the lowest total exchangeable calcium have the highest percentage of total calcium in exchangeable form, indicating the important function of colloidal material in conserving the supply of available calcium.

It is noticeable also that the two soils which have the highest content of colloid (Cove and Olympic) also have the highest percentage of exchangeable calcium. This is not necessarily true, however, when severe leaching has occurred. None of these soils are very acid and are not therefore extremely leached.

Retention of anions

The manner in which available anions are held in soils has not been fully determined. The phosphate ion has been most studied. Russell and Prescott (12) believe that physical adsorption occurs, since their data can be

TABLE 6
Exchangeable calcium

SAMPLES		pH	EXCHANGEABLE CALCIUM	PROPORTION OF TOTAL CALCIUM EXCHANGEABLE
			<i>per cent</i>	<i>per cent</i>
Chehalis Colloids				
Horizon	I.....	5.11	0.98	92.5
	II.....	5.60	0.89	84.8
	III.....	6.00	1.07	99.1
Chehalis Soil	I.....	5.48	0.34	8.3
	II.....	5.51	0.40	9.3
	III.....	5.51	0.41	10.6
Cove	I.....	5.61	0.46	20.2
	II.....	6.14	0.58	28.3
	III.....	6.12	0.65	22.0
Willamette	I.....	5.36	0.35	24.5
	II.....	5.36	0.24	19.2
	III.....	6.63	0.36	14.8
Dayton	I.....	5.48	0.28	15.0
	II.....	5.41	0.31	22.0
	III.....	5.95	0.47	23.3
Aiken	I.....	5.11	0.16	34.0
	II.....	5.09	0.14	50.0
	III.....	5.02	0.15	42.9
Olympic	I.....	5.26	0.55	18.2
	II.....	5.55	0.71	28.9
	III.....	5.78	0.67	29.4
Melbourne	I.....	6.14	0.25	56.8
	II.....	5.73	0.24	42.1

adapted to Freundlich's Adsorption Isotherm. Comber (4), Fisher (5), and Teakle (13), however, explain it as purely chemical precipitation. Roszman (11) thinks that organic matter may play an important part in taking up soluble phosphates. Other important anions are not taken up in as large quantities as the phosphate.

Retention of PO₄

The retention of the phosphate ion by both the soils and the separated colloids was studied. The ratio of the weight of the samples and the volume of solutions was kept at 1 to 10. The solutions used were made up from di-sodium phosphate and mono-potassium phosphate to give approximately neutral mixtures of the different phosphate concentrations.

The soils and the phosphate mixtures were allowed to stand in contact for three hours, with occasional stirrings. A little sodium chloride was then added as a flocculent, and in a few minutes aliquots of the clear supernatant solutions were taken for analysis.

The data show a large amount of phosphate retained by the colloid material. At the lower concentrations, retention is nearly complete. When retention amounted to around 5000 p.p.m., however, the colloid material seems to have been approaching its approximate capacity.

TABLE 7
Amount of PO₄ taken up by colloids

SOILS	CONCENTRATION OF PO ₄ IN SOLUTIONS USED							
	20	40	80	160	320	640	960	1280
	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.
Chehalis Colloids								
Horizon I.....	193	388	780	1,550	2,997	4,992	5,020	5,650
II.....	196	396	790	1,581	3,012	4,960	4,950	5,350
III.....	193	395	783	1,564	3,100	5,088	5,015	5,200

The curve for retention is a straight line up to 1550 p.p.m. at which point there is a slight break followed by a slight bend, and finally the curve again straightens.

Assuming that all exchangeable calcium found in the colloidal material should function to precipitate PO₄ ions, only about a third of the phosphate actually retained could be accounted for. Even after liberal allowance is made for the action of soluble iron and aluminum in precipitating phosphate there would yet remain a large amount not accounted for by chemical precipitation.

It seems probable, therefore, that the break in the curve may represent the point at which retention by chemical precipitation has been satisfied. Beyond this point retention is probably principally mechanical absorption in the interstitial spaces of the colloid matter. Phosphate so held should be rather easily removed from the soil.

Wiley and Gordon (14) found appreciable amounts of phosphate retained by silica gel, apparently a mechanical retention of the phosphate in the small pore spaces of the colloid. This retained phosphate could be washed out but with some difficulty.

Table 7 indicates that the soil as a whole has a much lower capacity for retention of phosphate than the colloidal material. The correlation between phosphate retention and percentage of colloid in the soil is not close however. Since the amount of the precipitating ions, of which calcium is doubtless very

TABLE 8
Amount of PO_4 taken up by soils from the following

SOILS	CONCENTRATION OF PO_4 IN SOLUTIONS USED							
	20	40	80	160	320	640	960	1280
	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.
Chehalis								
Horizon { I.....	150	289	456	503	1,120	1,440	1,872	2,104
II.....	165	309	452	598	1,286	1,984	2,100	2,100
III.....	180	339	473	600	1,125	1,716	1,800	2,097
Cove { I.....	191	383	603	920	1,762	1,880	2,052	2,250
II.....	193	384	705	960	1,660	1,600	1,900	2,048
III.....	194	372	635	880	1,441	1,472	1,953	1,850
Willamette { I.....	152	305	512	682	1,362	1,664	1,500	1,508
II.....	178	336	548	566	1,330	1,696	1,632	1,203
III.....	186	342	536	675	1,230	1,816	1,660	1,885
Dayton { I.....	169	313	512	682	1,180	1,408	1,550	1,550
II.....	190	348	548	740	1,488	1,792	1,752	2,050
III.....	188	342	536	720	1,444	1,748	1,648	1,813
Aiken { I.....	194	392	756	1,120	2,233	3,520	3,250	3,148
II.....	197	394	786	1,263	2,322	3,328	3,600	3,873
III.....	198	396	783	1,245	2,351	3,776	3,842	3,952
Olympic { I.....	191	380	655	905	1,708	2,816	2,652	2,950
II.....	188	397	655	878	1,600	2,400	2,450	2,160
III.....	186	360	604	773	1,536	2,272	2,355	2,280
Melbourne { I.....	193	388	608	974	1,662	2,528	2,350	2,200
II.....	197	393	650	1,018	1,400	2,560	2,308	2,402
Peat.....	158	355	645	980	1,931	2,240	2,650	2,888
Muck.....	196	392	873	1,382	2,868	2,960	4,250	4,900

important, varies considerably, lack of close correlation of phosphate retention with amount of colloid or any other single factor is not illogical.

From the above data it appears that organic matter in the peat soil is not especially effective in retaining phosphate. Muck which contains considerable mineral matter has a much higher retentive capacity. There is also a decided lack of correlation between phosphate retention and the percentage of

exchangeable calcium in the various soils, indicating again that precipitation of calcium phosphate is not the only important factor in phosphate retention. Other precipitating ions, the quantity of which is not known, are undoubtedly important factors in the phosphate retention. Some of the soils were rather high in iron and aluminum but how much came into the solution to combine with phosphate is not known.

TABLE 9
Available phosphate, phosphate retention, and the R_2O_3/SiO_2 ratio

SOILS	PO ₄ SOLUBLE IN 0.001 N H ₂ SO ₄	PO ₄ RETENTION FROM SOLUTION CONTAINING 1280 P.P.M. PO ₄	MOL. R ₂ O ₃ MOL. SiO ₂
	p.p.m.	per cent	
Chehalis			
Horizon { I.....	1.0	0.21	0.28
II.....	0.5	0.21	0.30
III.....	0.3	0.21	0.28
Cove { I.....	0.4	0.23	0.31
II.....	0.3	0.21	0.34
III.....	0.2	0.19	0.31
Willamette { I.....	2.8	0.15	0.18
II.....	0.5	0.12	0.19
III.....	0.3	0.19	0.20
Dayton { I.....	0.9	0.16	0.19
II.....	0.2	0.21	0.19
III.....	0.2	0.18	0.23
Aiken { I.....	0.2	0.32	0.42
II.....	Trace	0.33	0.41
III.....	Trace	0.23	0.38
Olympic { I.....	0.3	0.30	0.39
II.....	0.2	0.22	0.36
III.....	0.2	0.23	0.34
Melbourne { I.....	0.2	0.22	0.21
II.....	0.2	0.24	0.23

A study of the amount of phosphate (table 9), soluble in 0.001 *N* sulfuric acid in the untreated soils indicates a normally low availability. There appears to be no connection between the soluble phosphate in the soils and the retention of additional soluble phosphates. There does, however, appear to be some slight connection between soluble phosphate and the molecular ratio R_2O_3/SiO_2 . The Aiken and Olympic soils, which have a high ratio, show a low concentration of soluble phosphate, indicating that iron and aluminum may function

in rendering the native phosphates of the soil insoluble. This may be taken as some indication that the high ratio R_2O_3/SiO_2 may be correlated likewise to some extent with retention of the added soluble phosphate.

Regardless of what the specific relation may be, it is apparent that these soils have a high retentive capacity for the phosphate ion, and that this retentive capacity is rather intimately related to the colloidal fraction. It may likewise be concluded that little loss of soluble phosphates is likely to occur, even when the phosphates are added liberally to highly colloidal soils.

SUMMARY

1. The colloid content of nine soil series was determined by horizons and the colloid separated from each of the three horizons of one series for detailed study. The amount of colloid found varied from 20 to 65 per cent in the mineral soils.

2. The colloidal material was studied as to composition of Al_2O_3 , Fe_2O_3 , CaO , organic matter, pH, and exchangeable calcium, and compared with the whole soil.

3. Similar studies were made of each horizon of each of the other soils for comparison of physical properties with chemical composition.

4. All the soils behave similarly to the plastic or non-friable group used by Bennett (2) rather than to the friable or lateritic group. There is some slight lateritic tendency in the Aiken and Olympic series, however.

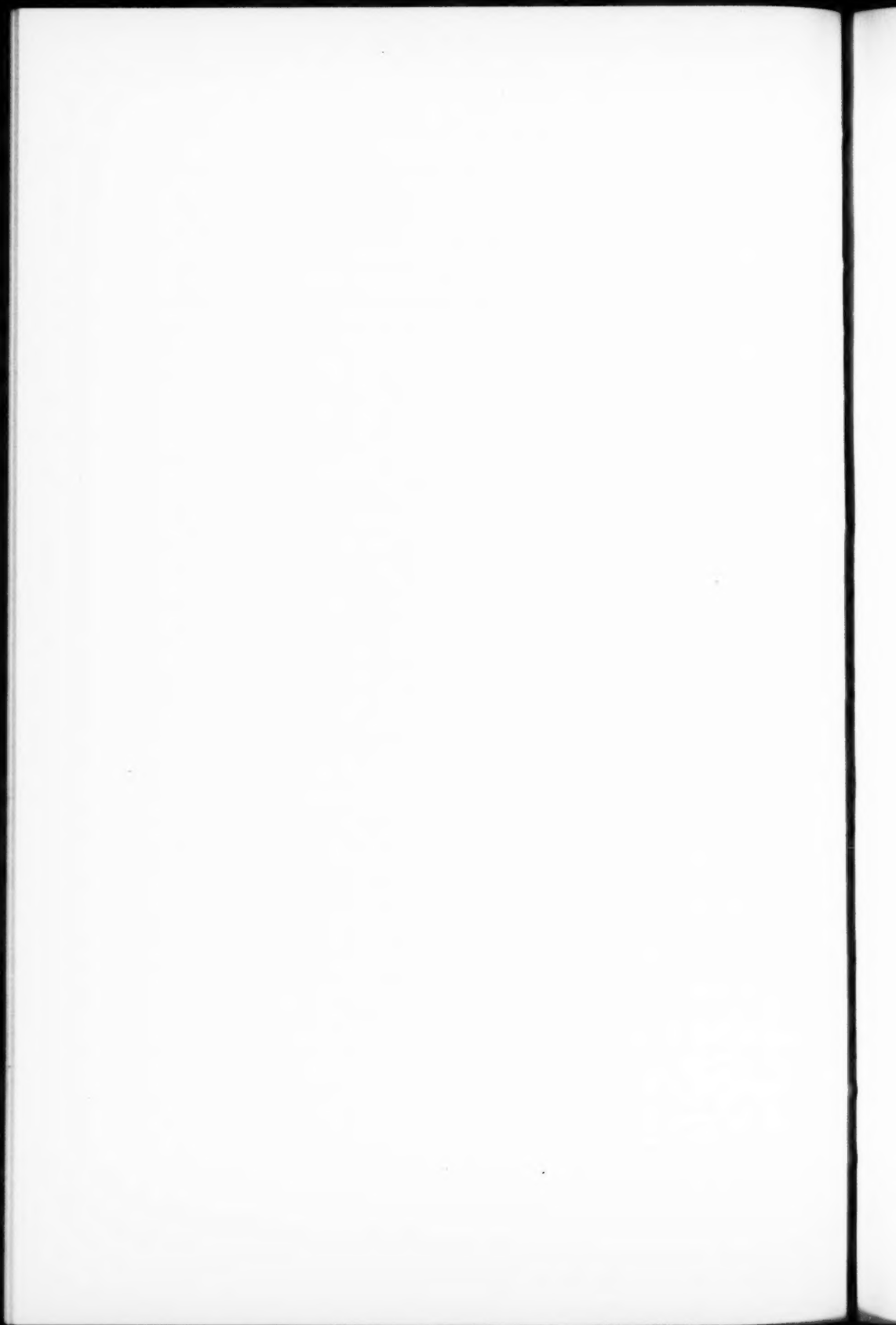
5. Both the separated colloids and the soils themselves show a high retentive capacity for soluble phosphates. The colloids show a higher retentive capacity than the whole soil.

6. There is not sufficient exchangeable calcium or other bases to account for the entire amount of phosphates retained by either the soils or the colloids.

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THE FERMENTATION OF GLUCOSE AND XYLOSE BY THE NODULE BACTERIA FROM ALFALFA, CLOVER, PEA, AND SOYBEAN

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Received for publication April 16, 1929

One of the recognized characteristics of the root nodule bacteria of the *Leguminosae* is the ability to ferment sugars. Although there are many reports concerning the change in reaction of a carbohydrate culture medium brought about by the growth of nodule bacteria, the quantitative data relating to this subject are meagre. Chronologically the first report is that of Mazé (5) in 1898, made in connection with his studies of nitrogen fixation by the organisms in artificial culture. In a medium containing approximately 2 per cent sucrose he found 59 to 68 per cent destruction of sugar in 19 to 22 days. In 1911-12 Fred (3) reported a limited fermentation of maltose and sucrose by various strains of the nodule bacteria; in no case was more than 20 per cent of the sugar utilized in one month's time. In a brief report on nitrogen-fixation by non-symbiotic organisms, Hutchinson (4) in 1922-23 presented a graph of glucose destruction by root nodule bacteria. The strain of this culture was not given. The curve indicates a rapid utilization of sugar in the first 10 days, the concentration falling from 2 per cent to less than 1 per cent during that time. Thereafter there is a gradual decrease in residual sugar until at 60 days approximately 0.4 per cent is left. More extensive tests were reported in 1928 by Anderson, Peterson, and Fred (1). These authors studied the rate of fermentation of glucose by two strains of root nodule bacteria of alfalfa in large cultures. They found that 0.435 gm. per 100 cc. were destroyed in 45 days by one strain and 0.6 gm. per 100 cc. in 41 days by a second strain.

The present work was undertaken to measure the rate at which a typical hexose, glucose, and a typical pentose, xylose, are destroyed by various species of root nodule bacteria and also to determine the total numbers of bacteria at various intervals.

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EXPERIMENTAL METHODS

The general procedure was to grow the organism in a medium consisting of dipotassium phosphate 0.5 gm., magnesium sulfate 0.2 gm., sodium chloride 0.2 gm., calcium sulfate 0.1 gm., carbohydrate 10 gm., yeast water (infusion) 100 cc., and distilled water, 900 cc. In certain experiments either 3 gm. of calcium carbonate or 3 gm. of basic slag (Thomas phosphate meal), was added. Basic slag was chosen because of its use in the fertilizer industry. The reaction was adjusted to a pH of 7.2-7.3. The media were sterilized at 120°C. for 20 minutes on two successive days before inoculation. Sugar determinations were made by the micro method of Shaffer and Hartmann as modified by Stiles, Peterson, and Fred (6). Before samples for quantitative analyses were drawn, purity tests on litmus milk and potato slopes were made.

In some cases where the destruction of sugar was very slow, the percentage of the carbohydrate apparently increased with the age of the culture. It was thought that the apparent increase was due to evaporation of the cultures. To test this assumption the flasks were weighed each time before and after the

TABLE 1
Effect of evaporation on the concentration of glucose in shallow layers of fermenting culture solutions

TIME	VOLUME	REMOVED FOR ANALYSIS	LOST BY EVAPORATION	GLUCOSE BY ANALYSIS	GLUCOSE CORRECTED FOR EVAPORATION
days	cc.	cc.	cc. per day	gm. per 100 cc.	gm. per 100 cc.
0	89.0			1.37	1.37
12	84.4	10.9	0.38	1.13	1.07
19	70.4	9.0	0.45	1.00	0.91
33	55.3	9.9	0.35	0.85	0.69

removal of the sample for analysis. From the data in table 1, column 4, it is seen that the loss of weight ranged from 0.35 to 0.45 cc. per day and averaged 0.381 cc. for 33 days. The total loss for the whole fermentation period of 33 days amounts to 12.5 cc. Obviously a correction for this amount of evaporation must be made for the concentration of the sugar. The percentages of sugar found by analysis (table 1, column 5) have been corrected for evaporation and the corrected figures are given in column 6. A comparison of these two columns shows that the apparent rate of glucose destruction is considerably slower than the actual rate.

All of the figures obtained by analysis were therefore corrected to the volume after inoculation and then expressed in terms of 100 cc. of culture.

The following pure cultures of root nodule bacteria were used:²

1. *Rhizobium meliloti*—Alfalfa (*Medicago sativa*)
2. *Rhizobium trifolii*—red clover (*Trifolium pratense*)
3. *Rhizobium leguminosarum*—pea (*Pisum sativum*)
4. *Rhizobium japonicum*—soybean (*Soja max*)

² The nomenclature is that proposed by Baldwin and Fred (2).

FERMENTATION OF GLUCOSE

In the preliminary experiment a few sugar determinations were made at intervals upon two cultures inoculated with *Rhizobium meliloti* No. 100. One culture contained calcium carbonate; the other did not. In both cases there was a gradual decrease in the amount of sugar present; about 10 per cent

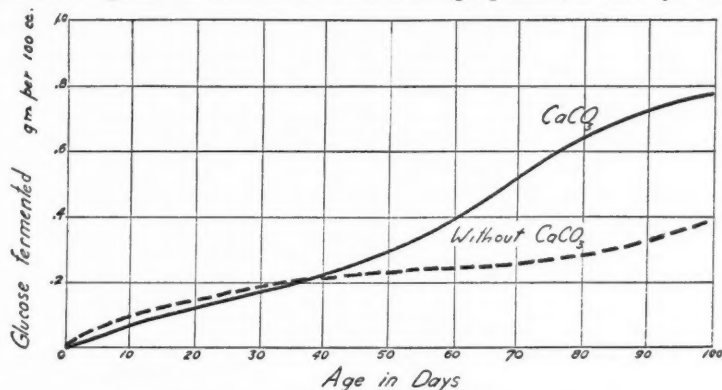


FIG. 1. THE FERMENTATION OF GLUCOSE BY RHIZOBIUM TRIFOLIUM IN A YEAST WATER MEDIUM

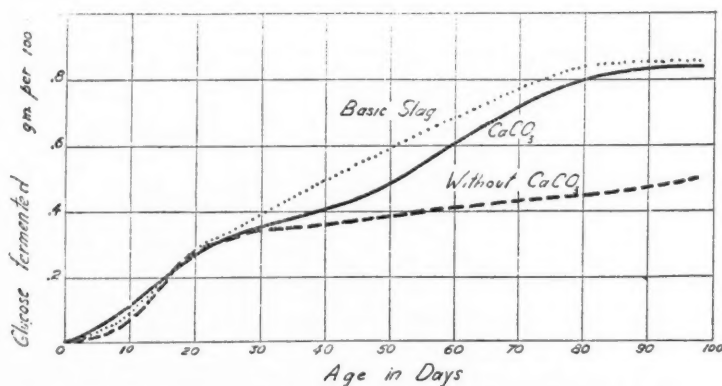


FIG. 2. THE FERMENTATION OF GLUCOSE BY RHIZOBIUM LEGUMINOSARUM IN A YEAST WATER MEDIUM

was destroyed in 20 days. In 60 days about 70 per cent of the sugar in the culture containing calcium carbonate was destroyed. After 100 days, about 20 per cent of the sugar in the culture without calcium carbonate was consumed and 90 per cent of the sugar in the culture with calcium carbonate. These results show that calcium carbonate is beneficial to the growth of the nodule organism.

In the first experiment 200 cc. of the medium in 750-cc. Erlenmeyer flasks were used and seeded with *Rhizobium trifolii* No. 205. The results of this experiment are shown graphically in figure 1.

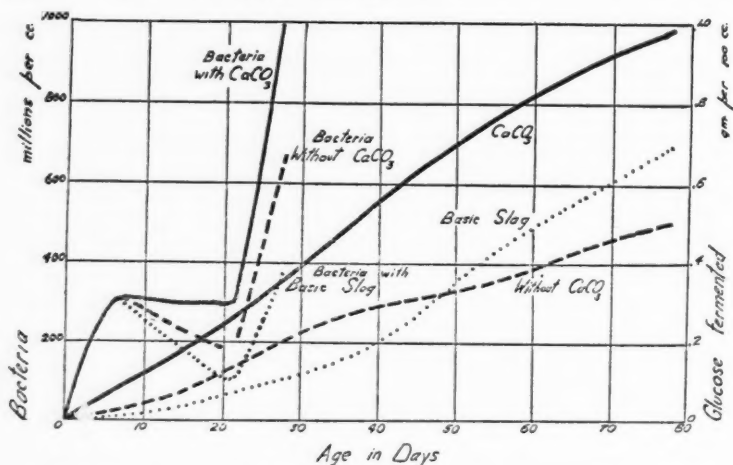


FIG. 3. THE FERMENTATION OF GLUCOSE BY RHIZOBIUM JAPONICUM IN A YEAST WATER MEDIUM

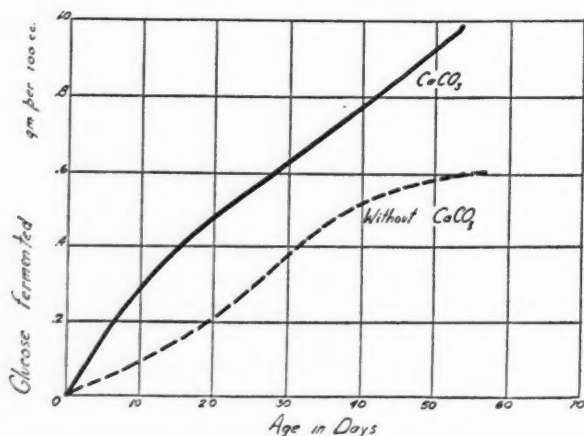


FIG. 4. THE FERMENTATION OF GLUCOSE BY RHIZOBIUM MELILOTI IN A YEAST WATER MEDIUM

In experiment 2, the medium was made up without the glucose and the percentage of the salts doubled. The sugar was then made in a separate water solution and, after autoclaving, 50 cc. of each solution were pipetted into

750-cc. Erlenmeyer flasks. The cultures were inoculated with *Rhizobium leguminosarum* No. 308, *Rhizobium japonicum* No. 504, and *Rhizobium meliloti* No. 100. The data are given in figures 2, 3, and 4.

The following conclusions may be drawn from these data:

The fermentation of glucose is a slow but continuous process without any very marked difference between the cultures studied. The representative of the alfalfa group is perhaps the most active, whereas that of the clover group is the weakest in relation to the sugar destroyed.

If the rate of glucose fermentation of the various cultures be compared it will be seen that the clover and pea bacteria are much alike. The alfalfa and soybean bacteria behave somewhat differently and fail to show any marked decrease in fermentation with an increase in age of culture.

A neutralizing agent practically doubles the quantity of sugar destroyed. Without CaCO_3 , from 40 to 50 per cent of the glucose was destroyed; and with CaCO_3 , the figures are from 70 to 90 per cent.

In the early stages of the fermentation the rate is approximately as rapid in the absence as in the presence of CaCO_3 . Presumably an accumulation of acid produces such a high hydrogen-ion concentration in the absence of CaCO_3 that the continued destruction of sugar is checked. Basic slag shows about the same effect as CaCO_3 . Apparently its action is due to its neutralizing power and not to its phosphorus content.

Because of the limited number of determinations and the difficulty in securing satisfactory counts of the numbers of bacteria, conclusions can be drawn only with considerable reservation. The maximum number was reached in about 7 days, but in some cases a second high point was observed after 28 days.

FERMENTATION OF XYLOSE

The data dealing with the destruction of this sugar are given graphically in figures 5, 6, 7, and 8.

If the same length of fermentation period is chosen, there is no appreciable difference in the degree of fermentation of glucose and xylose. Likewise, there is no particular difference in the rate at the time of maximum fermentation. After the maximum rate is reached the fermentation of xylose shows the same gradual decrease with an increase in the age of the culture that was observed with glucose. Apparently the pentose sugar is just as good a source of carbon as the more common hexose.

Although the alfalfa organism is the most active in the fermentation of glucose, it is the slowest fermenter of xylose. The other three organisms ferment the pentose at about the same rate.

As was noted with glucose, a neutralizing agent increases the percentage of sugar destroyed. That this is entirely a question of reaction is shown by the rate of sugar destruction in the early stages of the fermentation; up to 10 days, approximately the same quantity of sugar is destroyed in the presence as in

the absence of CaCO_3 . Although there are minor variations, they have no particular significance.

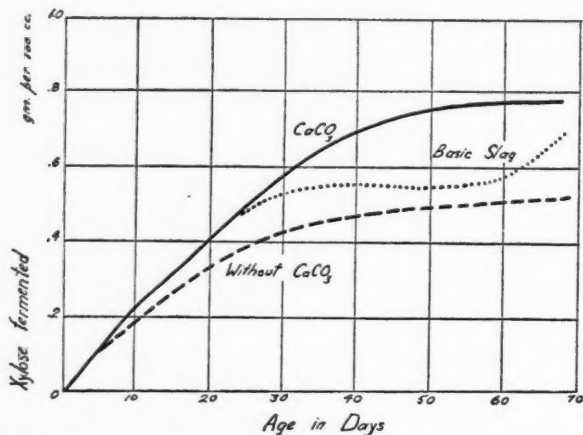


FIG. 5. THE FERMENTATION OF XYLOSE BY RHIZOBIUM TRIFOLII IN A YEAST WATER MEDIUM

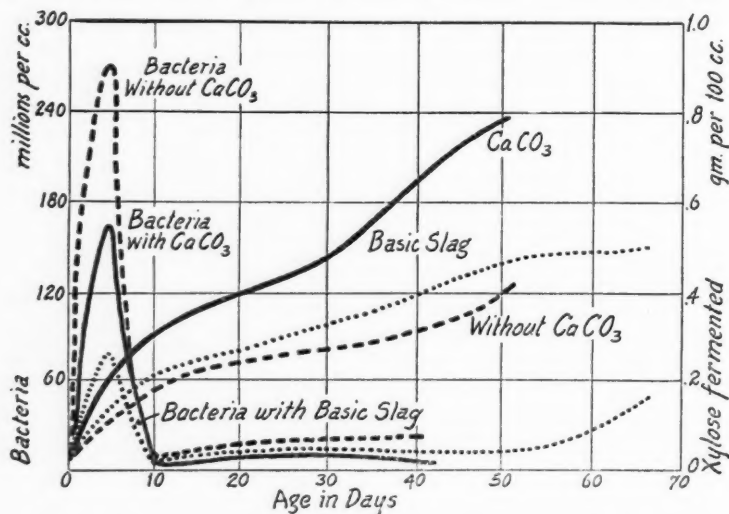


FIG. 6. THE FERMENTATION OF XYLOSE BY RHIZOBIUM LEGUMINOSARUM IN A YEAST WATER MEDIUM

H-ion determinations on the unneutralized cultures at the end of the fermentation give further evidence to explain the slow fermentation. Without CaCO_3 or basic slag in a xylose medium, pH values for the different microorganisms

were found as follows: *Rhizobium meliloti*, 5.6; *Rhizobium trifolii*, 5.0; *Rhizobium japonicum*, 4.6. The pH values in a glucose medium were: *Rhizobium meliloti*, 5.2; *Rhizobium trifolii*, 5.4; and the *Rhizobium leguminosarum*, 5.6.

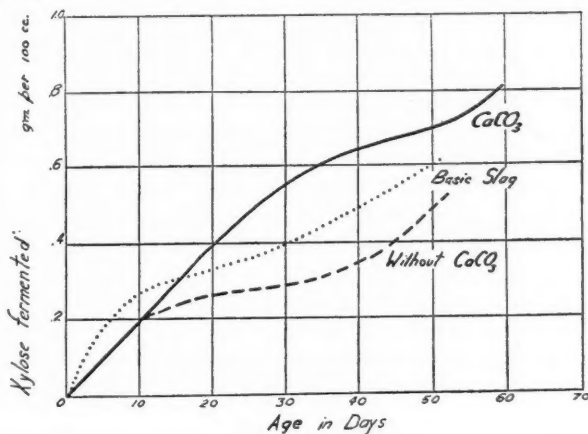


FIG. 7. THE FERMENTATION OF XYLOSE BY RHIZOBIUM JAPONICUM IN A YEAST MEDIUM

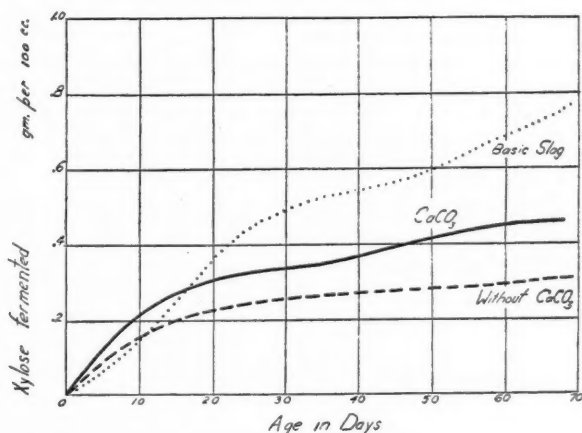


FIG. 8. THE FERMENTATION OF XYLOSE BY RHIZOBIUM MELILOTI IN A YEAST WATER MEDIUM

As was observed in the fermentation of glucose, a maximum in the numbers of bacteria was reached in about seven days. In many cases a second maximum point was observed, but at a slightly later date than with glucose. The variation in the numbers of bacteria may be explained in part by the frequently observed formation of a thick gum which makes it difficult to break up the clumps of organisms.

SUMMARY

1. Laboratory experiments on the rate of sugar destruction by four species of nodule bacteria, *Rhizobium meliloti*, *Rhizobium trifolii*, *Rhizobium leguminosarum*, and *Rhizobium japonicum* in yeast water carbohydrate media were conducted. A typical hexose, glucose, and a typical pentose, xylose, were used.

2. Cultures of *Rhizobium meliloti*, *Rhizobium trifolii*, *Rhizobium leguminosarum*, and *Rhizobium japonicum*, when grown in a sugar medium with calcium carbonate or basic slag present, show a greater destruction of sugar than in a similar medium without these basic substances. In the presence of these substances approximately three-fourths of the sugar was destroyed in 75-day-old cultures, whereas in a medium without these substances only one-half of the sugar was destroyed in the same time.

3. The rate of fermentation of glucose and xylose each day is usually faster in the young cultures, showing a gradual decrease with an increase in age.

4. As a rule the maximum number of bacteria is reached within 10 days. In some cases there were several successive increases and decreases in numbers.

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BOOK REVIEWS

REVIEWS OF AND REFERENCES TO BOOKS OF INTEREST TO THE READERS OF SOIL SCIENCE

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Received for publication July 24, 1929

Dictionary of Bacteriological Equivalents. By WILLIAM PARTRIDGE. Baillière, Tindall, and Cox, London; and Williams & Wilkins Company, Baltimore, 1927. Pp. xi + 141.

A very convenient reference book for microbiologists, biochemists, and biologists. The equivalents given are French-English, German-English, Italian-English, and Spanish-English.

Lectures on Plant Pathology and Physiology in Relation to Man. W. B. Saunders Company, Philadelphia and London, 1926-27. Pp. 207, figs. 16.

This contains (a) a group of lectures on plant pathology and physiology in relation to man, given during the autumn and winter of 1926-27 under the auspices of The Mayo Foundation and the local chapter of Sigma Xi at Rochester, Minn.; the Medical School of the University of Wisconsin, Madison, Wis.; the Graduate School of the University of Minnesota, Minneapolis, Minn.; the Graduate School of the University of Iowa, Iowa City, Iowa; the Iowa State College, Ames, Iowa; and the Des Moines Academy of Medicine, Des Moines, Iowa. The authors of these lectures were Louis Otto Kunkel, Henry Chandler Cowles, George Herbert Coons, Elvin C. Stakman, Herbert Hice Whetzel, and Winthrop John Vanleuven Osterhout.

Soil Characteristics. By PAUL EMERSON. McGraw-Hill Book Company, New York, 1925. Pp. x + 222, pls. 1, figs. 5.

The book deals with physical, chemical, and microbiological methods involved in the study of soils.

Handbook of Fertilizers. By A. F. GUSTAFSON. Orange Judd Publishing Company, Inc., New York; and Kegan Paul, Trench, Trübner & Co., Ltd., London, 1928. Pp. 122, figs. 18.

As stated by the author, "This little book is an attempt to supply accurate, up-to-date information as to the source and make-up of commercial fertilizers. Special stress is laid on the effects of fertilizers on soils and crops in the hope of aiding the user to make a wise choice for his individual soil conditions."

The Economics of Land Reclamation in the United States. By RAY P. TEELE. A. W. Shaw Company, Chicago and New York; and A. W. Shaw and Company, Ltd., London, 1927. Pp. xv + 337.

In this book is presented a discussion of the experience of the United States in the reclamation of land for agricultural use, with occasional reference to the experience of other countries in this field. The subject is discussed from the economic standpoint rather than from the engineering or the cropping standpoint, although it is necessary to consider both engineering and crop production, since crop production is the object of land reclamation and engineering is the means of accomplishing this objective.

Phosphoric Acid, Phosphates, and Phosphatic Fertilizers. By WM. H. WAGAMAN assisted by HENRY W. EASTERWOOD. The Chemical Catalog Company, Inc., New York, 1927. Pp. 370, figs. 58.

The book contains a mass of valuable information and is well supplied with references.

Foundations of Silviculture upon an Ecological Basis, volume I. By JAMES W. TOUMEY. John Wiley & Sons, Inc., New York; and Chapman & Hall, Ltd., London, 1928. Pp. xxv + 438, figs. 11.

The author discusses in chapters I to X the site factors, and in chapters XI to XV the forest. The book is well written and should be given a place on the shelves of every reader interested in soils and their products.

The Practice of Silviculture. By RALPH C. HAWLEY. John Wiley & Sons, Inc., New York; and Chapman & Hall, Ltd., London, 1929. Second edition, pp. xiii + 335, figs. 69.

The book deals with applied silviculture. It is well illustrated and contains an appendix of forest terminology.

Minerals in Pastures and Their Relation to Animal Nutrition. By J. B. ORR assisted by HELEN SCHERBATOFF. H. K. Lewis & Co., Ltd., London, 1929. Pp. x + 150, figs. 2.

Within recent years much new information has become available on the composition of forage crops and of pasture grasses in particular. Much of this new information is summarized in this book.

Handbook of Microscopical Technique. Edited by C. E. MCCLUNG. Paul B. Hoeber, Inc., New York, 1929. Pp. xiv + 495, figs. 43.

A number of leading authorities have collaborated in creating a valuable treatise. As noted in the preface, "In two previous texts, *General Cytology* and *Special Cytology*, edited by Dr. Cowdry, experts in various fields of biology have presented the results of their investigations. In the present work, which extends the series, the methods involved in these and similar studies are given."

Chemistry in Medicine. Edited by Julius Stieglitz. The Chemical Foundation, Inc., New York. Pp. xxi + 757, pls. 9, figs. 15, chart 1.

The Chemical Foundation is to be felicitated on having got out this book and on having made the information contained in it widely available.

Field-Crop Enterprises, Including Soil Management. By KARY C. DAVIS. J. B. Lippincott Company, Philadelphia, London, Chicago, 1928. Pp. vi + 528, figs. 260.

We are informed by the author that the book is intended primarily as a text in vocational schools. At the same time, it should also prove helpful to progressive farmers, since it offers in a compact and popular way information of wide interest.

Scientific Preservation of Food. By THOMAS M. RECTOR. John Wiley & Sons, Inc., New York; and Chapman & Hall, Ltd., London, 1925. Pp. xi + 213.

There is much in this book that will interest microbiologists. The author points out in the preface that: "For the past 12 years the writer has been engaged in applying the principles of chemistry and bacteriology to the problems of the food manufacturing industry. This experience has included extensive analytical work, solution of spoilage problems, and finally the creation of new products and processes."

Botany. By WILLIAM J. ROBBINS AND HAROLD W. RICKETT. D. Van Nostrand Company, Inc., New York, 1929. Pp. xxiii + 535, figs. 384.

The intimate relations that exist between plant and soil science will justify the student of soils in reading this book carefully.

Ackerbaulehre, volume 2. Edited by TH. ROEMER. Paul Parey, Berlin, 1929. Pp. xvi + 564, colored pls. 4, figs. 130.

This work represents an ambitious effort on the part of the editor and his associates to cover much of the field of soil science. Part I deals with the origin, properties, and classification of soils; part II, with the biology of soils; part III, climate in its agricultural relations; part IV, reclamation methods; part V, tillage; part VI, seed, germination, and quality of seed; part VII, feeding and fertilization of plants; part VIII, the control of weeds; part IX, catch crops and green manures; part X, diseases of plants; and part XI, crops and their storing and conservation.

Die Untersuchung und Begutachtung von Düngemitteln, Futtermitteln, Saatwaren und Bodenproben. By PAUL KIRSCHKE assisted by ALBERT KABITZSCH. Paul Parey, Berlin. Second edition, pp. xxii + 386.

The book is devoted largely to a consideration of analytical methods employed in the German agricultural experiment stations for ascertaining the composition of fertilizers, feeding stuffs, and soils. Methods are also described for determining the quality of agricultural seeds.

Handbuch der Bodenlehre, volume I. Edited by E. BLANCK. Julius Springer, Berlin, 1929. Pp. viii + 335, figs. 29.

As is indicated on the title page, the book deals with the principles involved in the genesis of soils. The editors tell us in the preface that, in dealing with soil science, account must be taken of other sciences, such as botany, tillage, and climatology. An attempt has been made by the collaborators to outline the broad limits of the field. The discussion follows in logical sequence, and should interest not only the student of soils, but also all progressive landowners.

